Structural Preferences and Applications of Ruthenium-Porphyrin complexes - A Mini Review

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Abstract: Ruthenium complexes are known in huge numbers and possesses diverse structural features and wide range of applications. This is due to the ability of ruthenium to form complexes with different oxidation states like the common +2, +3, +4. Other oxidation ststes of ruthenium like +6 and +7, +8 also possible. Here we have reviewed the ruthenium-porphyrin complexes with different oxidation of ruthenium like Ru(II), Ru(III) and Ru(IV). The synthesis, geometrical, electronic structure, spectral properties and reactivities of important ruthenium-porphyrin complexes are covered. The octahedral geometry around ruthenium with axially disposed ligands like in these ruthenium porphyrin complexes with ligands like $N(Ph)_2$ (1), NH_3 (2), PH_3 (3) and AsH_3 (4), F (5), Cl (6), Br (7), I (8) have also been confirmed by theoretical DFT (BP86/Def2-TZVP) investigations. Due to the important applications of ruthenium-porphyrin complexes like in cancer chemotherapy through photodynamic therapy of like Thus this quantum chemical study can lead to design and find out the better ruthenium-porphyrin complexes with different ligands.

Keywords: Ruthenium; Porphyrin;Ru(II); Ru(III); Ru(IV); Cancer Chemotherapy; Catalysis;

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1. Introduction

Ruthenium chemistry is fast growing area of research because of its unique electronic structural arrangement ($4d^7\ 5s^1$). A significant element in the periodic table, ruthenium (atomic number 44) exhibits oxidation numbers 0 to +8 and -2, among which the +2, +3 and +4 are more common. Thus, ruthenium shows diverse structural preferences and wider applications. Porphyrin, on the other hand, very important molecule with potential applications. The ruthenium-porphyrin hybrid can play a vital role in the development of applied chemical sciences. The ruthenium cations with porphyrin, can mimic the role of metal-porphyrin complex and lead to diverse applications. Ruthenium-centred complexes are being researched for possible anticancer properties. [1, 2] Compared with platinum complexes, those of ruthenium show greater resistance to hydrolysis and more selective action on tumours. Ruthenium-based compounds have been used for light absorption in dye-sensitized solar cells, a promising new low-cost solar cell system.

2. Ru(II)-Porphyrin Compounds

In general, the free-base analogue reacts with a metal salt (or complex) in an organic solvent like DMF, chloroform, or toluene to metalate porphyrins (Por). The distortion that the rather rigid porphyrin ring must go through in order to permit the creation of the initial bond of an internal pyrrolenine nitrogen to the metal appears to be rate-limiting, which is the main cause of the high activation barrier and generally delayed metalation.[1] This also applies to the insertion of ruthenium. As low-spin air-stable biomimetic models of Fe(II) porphyrins, ruthenium porphyrins were first created. Adducts and intermediates (such as those comprising oxygen) should be more stable and inert for ruthenium than for iron compounds.[2–4] Ru-porphyrins have been studied as sensors and catalysts, particularly for oxidation processes. [5-7] The conditions for ruthenium insertion are far more stringent than those for iron in simple free-base neutral porphyrins [such as TPP, OEP, and others], usually requiring high temperatures and lengthy reaction periods.[8] Furthermore, ruthenium is only added to porphyrins as the Ru^{II}–CO fragment, producing neutral products of the form Ru(CO)(Por), in contrast to iron but comparable to osmium [9]. There are no known instances of "bare" Ru^{II}/Ru^{III} ions or other RuL or RuL_2 fragments being directly inserted. One could argue that a strong π-acceptor ligand, like CO, is required to remove a portion of the charge density that the $Por_2–$ macrocycle provides from the relatively soft metal ion like ruthenium(II) or osmium(II)). Indeed, in line with a significant contribution from π-back donation, the CO stretching mode in Ru(CO)(TPP) is observed at relatively low frequencies, approximately 1930–1945 cm^{-1}, depending on the source.[10–12] The axial coordination site opposite to CO is generally occupied by a weak and labile solvent molecule resulting from the process,[11] which can be readily substituted by a more potent σ and/or π-donor ligand (e.g. pyridine, imidazole).[13–15] The axial Ru–N bond exhibits considerable strength and stability.[16] Consequently, Ru-porphyrins and pyridyl ligands have been extensively utilized as fundamental components in the assembly of supramolecular structures.[17–19] The coordinated CO can be eliminated through continuous photolysis in solvents (S) with weak coordination, leading to the formation of $Ru(Por)(S)_2$ adducts.[20] In a similar manner, Ru(OEP)(CO)(py) in a degassed pyridine solution undergoes photochemical transformation to $Ru(OEP)(py)_2$.[21] In contrast, strong σ-donor and π-acceptor ligands such as phosphines (P) can easily displace the CO ligand from the original Ru(CO)(Por) under mild conditions, resulting in the formation of $Ru(Por)(P)_2$ derivatives.[22,23]

The six-coordinate ruthenium(II) porphyrin complexes, (OEP)Ru(CO)(Q), where OEP stands for 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion and Q represents either quinoline

(Qnl) or quinine (QN), have been synthesized from (OEP)Ru(CO) and characterized using MS, IR, UV–visible, and ^{1}H NMR spectroscopy.[24] The X-ray crystal structure for (OEP)Ru(CO)(Quinoline) has been established, showing that quinoline coordinates to the ruthenium through the nitrogen atom. The crystal packing of (OEP)Ru(CO)(Qnl) indicates that the Qnl groups of neighboring porphyrins are aligned relatively parallel to one another at a distance of 3.30 Å, suggesting a notably strong π-π interaction. Additionally, the X-ray crystal structure for (OEP)Ru(CO) was determined, which showed that water is coordinated to the ruthenium center. By analyzing the spectroscopic data for (OEP)Ru(CO), (OEP)Ru(CO)(Quinine), and (OEP)Ru(CO)(Quinoline), it was concluded that quinine likely binds to Ru via the nitrogen atom of the quinoline group. The redox properties of the complexes were examined using cyclic voltammetry at a Pt working electrode in a CH_2Cl_2 solution with NBu_4PF_6 as the supporting electrolyte, which indicated that the oxidations are centered on the porphyrin.[25] New anticancer drugs were created using metals other than platinum. Ruthenium complexes in the +2 and +3 oxidation states have drawn the most attention of all the metal derivatives that have been studied so far as promising substitutes for Pt(II)-based ones [26-31].

The restricted aqueous solubility and short in vivo half-lives of metallo-drugs have hindered their therapeutic applicability when supplied via standard intravenous techniques. This has led to low accumulation in tumor masses and inadequate bioavailability. As a result, a number of methods have been put out to deal with these problems, especially those that rely on nanotechnology [32-35]. High stability, significant loading capacity, and the potential for controlled or prolonged drug release are the primary benefits of employing nano-systems for drug delivery. This method can target certain tumor areas, limits sensitivity to chemical and/or enzymatic degradation, considerably lengthen the body's circulation duration, and lessen the harmful side effects of medication administration [26,35-40]. Recent overviews have provided an in-depth overview of the production, encapsulation into various nanosystems, and mechanism of action investigations of Ru(II)-based complexes [41, 42].

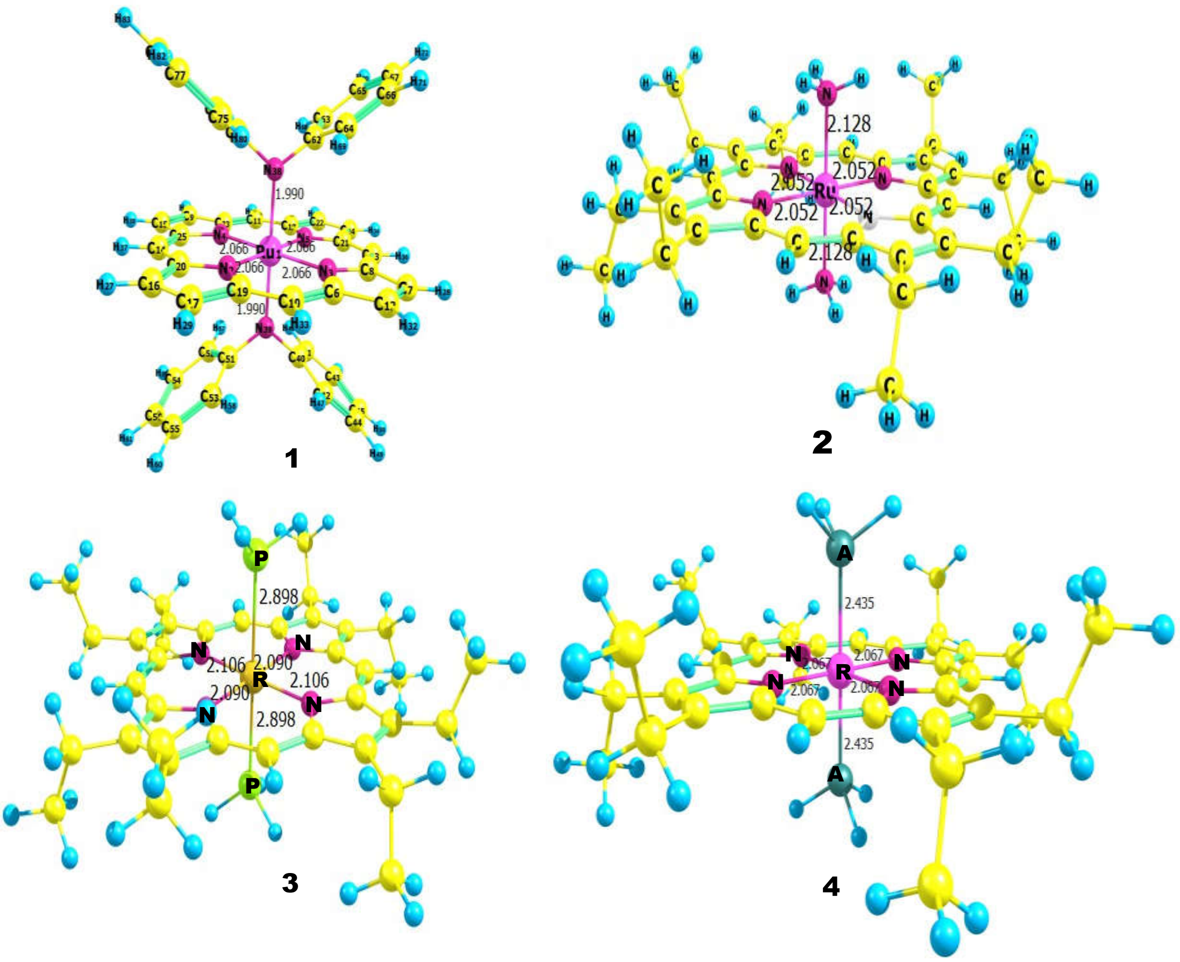
3. Ru(III)-Porphyrin Compounds

Ru(III)-porphyrin complexes are nown since 1984. The first reported ruthenium(III) porphyrin complex is Ru(OEP)(PPh_3)Br. The X-ray crystal structure of Ru(OEP)(PPh_3)Br reveal that ruthenium is displaced 0.049 Å from the plane of the pyrrole N atoms towards the phosphine. The Ru(OEP)(py) Br and [Ru(OEP)(py)CH_3CN]PF_6 complexes were also synthesized from Ru(OEP)(CO)py. The synthesised ruthenium(III) complexes are found to be low-spin from the magnetic and esr data. The six-coordinate ruthenium(II1) products have magnetic susceptibilities in the range of 1.9-2.3 BM, confirming the expected one unpaired electron in low-spin d^5 systems.[47] Arylruthenium(III) porphyrins are highly active catalysts for hydrocarbon oxidation. [48] The ruthenium(III) porphyrin, $[Ru^{III}(TDCPP)(Ph)(OEt_2)]$ (H2TDCPP = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin), is used as a catalyst for the oxidation of C−H bonds of various hydrocarbons with at room temperature gave alcohols/ketones in up to 99% yield within 1 hour. The chlorinated porphyrin TDCPP, which is a sterically encumbered porphyrin ligand, was stable in the presence of excess PhLi. We prepared $[Ru^{III}(TDCPP)(Ph)(OEt_2)]$ in 66% yield by treating $[Ru^{IV}(TDCPP)(Cl)_2]$ with excess PhLi (Scheme 1; similar to the synthesis of $[Ru^{III}(OEP)(Ph)(THF)]$) followed by column chromatography. Efforts were made to change the TDCPP ligand to its fluorine counterpart, namely, TDFPP, and $[Ru^{III}(TDFPP)(Ph)(OH_2)]$ was prepared in 73% yield from the reaction of $[Ru^{III}(TDFPP)(Cl)(THF)]$ and PhLi. The solid forms of $[Ru^{III}(TDCPP)(Ph)(OEt_2)]$ and $[Ru^{III}(TDFPP)(Ph)(OH_2)]$ are stable in air and light for at least one month and they can be purified by neutral alumina using CH_2Cl_2/hexane as eluent. These three complexes were characterized by X-ray crystallography. [48]

During the preparation of $Ru(OEP)(C_6H_5)_2$ by reaction of $Ru(OEP)Cl_2$ with C_6H_5Li/THF; following crystallization and column chromatography, Ru-$(OEP)(C_6H_5)_2$ is obtained in ca. 30% yield. It is found that the mother liquor of the crystallization contains a substantial amount of $Ru(OEP)(C_6H_5)$, so the $Ru(OEP)(C_6H_5)_2$ synthesis reaction also provides 50% yield of the monophenyl complex $Ru(OEP)(C_6H_5)$, possessing a Ru^{III} center (low-spin d^5). [49] The electrochemistry of $Ru(OEP)(C_6H_s)$ is comparatively simple. The cyclic voltammetric response of $Ru(OEP)(C_6H_5)$ reveals a one-electron (reduction) couple at -0.8 V one-electron (oxidation) couple at +0.48 V. [49]

4. Ruthenium(IV)-Porphyrin Compounds

Ruthenium-porphyrine complexes are existing in +2, +3 and +4 with oxidation states of ruthenium, among which the most common and stable oxidation state is +3 oxidation state followed by +4. Ruthenium(IV)-porphyrins also possess potential applications in the fields like cancer chemotherapy and catalysis. The unique structural features of these ruthenium(IV)-porphyrins also have applications as molecular rotors and switches. [50] The neutral ruthenium(IV)-porphyrin and their different complexes $RuP(NPh_2)_2$, (1), $RuP(NH_3)_2$, (2), $RuP(PH_3)_2$, (3), $RuP(AsH_3)_2$, (4) have been studied using computational methods. [51] The DFT(BP86/Def2-TZVP) optimized geometries of $RuP(NPh_2)_2$, (1), $RuP(NH_3)_2$, (**2**), $RuP(PH_3)_2$, (**3**), $RuP(AsH_3)_2$, (**4**) (where P = Porphyrin) along with their HOMO and LUMO orbitals are provided in the Figures Figure1 to Figure-1.



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2

3

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Figure 1. The DFT(BP86/Def2-TZVP) optimized geometries of RuP(NPh_2)$_2$, (1), RuP(NH_3)$_2$, (2), RuP(PH_3)$_2$, (3), RuP(AsH_3)$_2$, (4)

The feasibility of the ruthenium(IV)-porphyrins with axially substituted halogens also explored computationally and the results show the moderate stability of these compounds in their triplet state. 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) are provided in Figure 2. The DFT (BP86/Def2-TZVP) optimized geometries of the ruthenium(IV)-porphyrin 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.

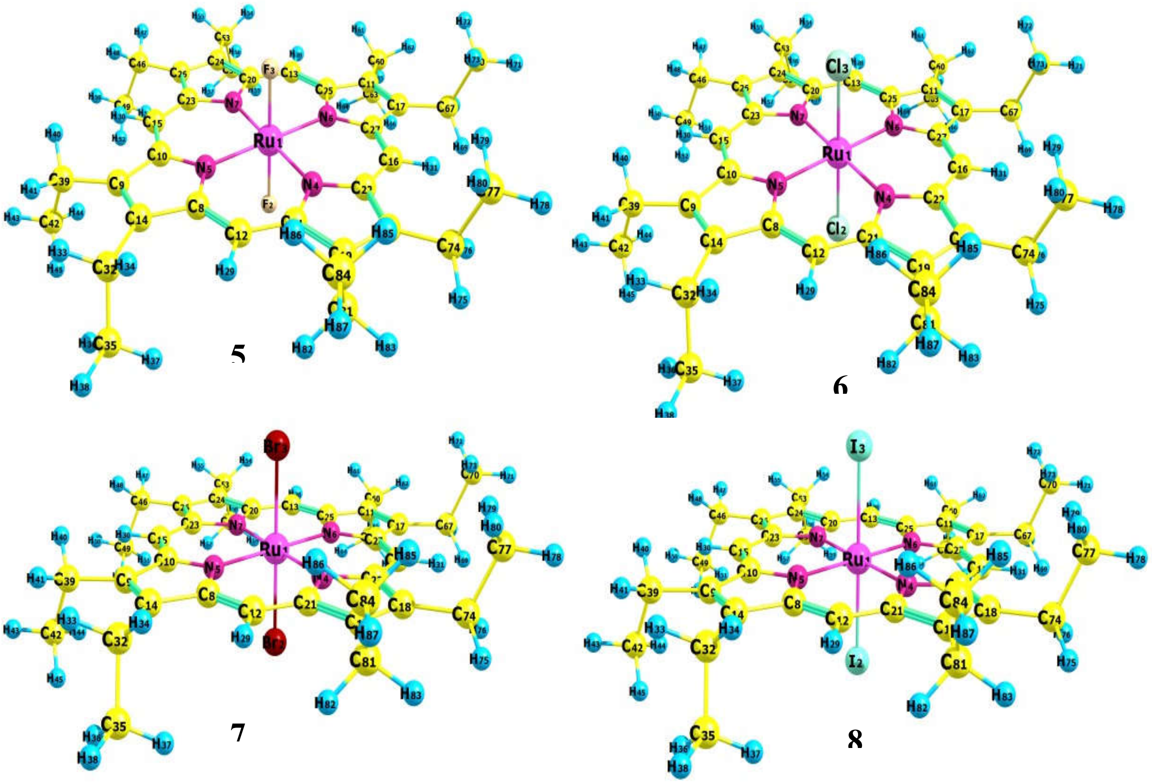

Figure 2. DFT (BP86/Def2-TZVP) optimized geometries of halogen substituted compounds 5-8 in their triplet state RuP(F)$_2$, (5), RuP(Cl)$_2$, (6), RuP(Br)$_2$, (7), RuP(I)$_2$, (8) (where P = Porphyrin)

Thus the DFT (BP86/Def2-TZVP) computed $E_{LUMO-HOMO}$ value of greater 2.0 eV of the compounds suggests the more stable nature and the viability of these compounds.

5. Ruthenium(VI)-porphyrins Compounds

Dioxoruthenium(VI) porphyrin is an example for the ruthenium-porphyrin existing in its +6 oxidation state which has two double bonded oxo ligands attached to the central ruthenium atom. This dioxoruthenium(VI)-porphyrin is known as powerful oxidant and having applications in catalysis. Other ruthenium(VII) and Ruthenium(VIII) porphyrins are unknown so far due to their unstable nature.

6. Conclusions

Ruthenium-porphyrin compounds are playing important role as in the cancer chemotherapy through photodynamic therapy, catalysis, drug delivery agents, molecular rotors, etc., Ruthenium forms ruthenium-porphyrin complexes in different oxidation states like stable +2, +3, +4 and among which +3 oxidation state is common and more stable whereas +4 oxidation often forms neutral ruthenium-porphyrin molecules. Other oxidation states for ruthenium like +6, +7 and +8 also possible. Here we have reviewed the existing ruthenium-porphyrin compounds in its different oxidation states and their importance in different fields. Further their synthesis also discussed to some extent. The ruthenium-porphyrin chemistry is growing in different directions like developing materials for different applications, forming macrocycles, in the field of catalysis, medical field, etc., The varying oxidation states of the ruthenium metal results in diverse ruthenium-porphyrin complexes which show wider structural preferences and the field has become one among the important research fields. Many structural aspects of the ruthenium-porphyrin complexes are still in need of deeper insight through experimental and computational research.

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