Research Article

Exploring the Ruthenium-Ligands Bond and Their Relative Properties at Different Computational Methods

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We report some experimental bond distances and computational models of six ruthenium bonds obtained from DFT to higher computational methods like MP2 and CCSD. The bonds distances, geometrical RMSD, and the thermodynamic properties of the models from different computational methods are similar. It is observed that optimization of molecules of many light atoms with different functional methods results in significant geometrical variation in the values and order of the computed properties. The values of the hyperpolarizabilities, HOMO, LUMO, and isotropic and anisotropic shielding are found to depend greatly on the type of the functional used and the geometrical variation rather than on the nature of basis set used. However, all the methods rated modelled Ru-S, Ru-Cl, and Ru-O bonds as having the highest hyperpolarizabilities values. The infrared spectra data obtained from the different computational methods are significantly different from each other except for MP2 and CCSD which are found to be very similar.

1. Introduction

Ruthenium complexes have received significant consideration as conductive, optical, anticancer, and antibiotic applications [1–16]. Besides great number of ruthenium complexes, there are many of the ruthenium-ligand bonds which are found relevant to their biological activities. The covalent bonding between Ru and N7 (guanine) is considered the predominant mode of action with DNA for Ru antitumor compounds [17–19]. It was also assumed that metals can form chelates with N7 and O6 atoms of guanine [20]. The formation of a hydrolyzed Ru-O bond is very significant for the activation of ruthenium complexes for biological activities [19, 21]. The rate of hydrolysis has significant effect on the anticancer activities [22–24]. Ruthenium has also been reported to bind to S of Cys. residue of Cathepsin B [25–27]. Mostly for Ru anticancer activities, bonding between Ru and N7 (guanine) is considered to be the predominant mode of action with DNA [17]. However, it is also possible that binding to guanine N7 atoms is less important than other types of interaction like interaction with phosphate groups, hydrogen bonds, and so forth [28].

The computational approach is very significant for the optimization of the complexes and design of novel complexes for various applications, studying their electronic, conductive, and spectroscopic properties in relation to their stability. However, it is computationally expensive to compute the properties of ruthenium complexes using higher basis set like aug-cc-pVTZ and high perturbation method like MP2. It is therefore highly important to optimize the computational methods which are affordable for the ruthenium complexes. In this paper, we have presented different models of ruthenium complexes which are different by the type of the ruthenium-ligand (Ru-L) bonds. The types of the Ru-L bond of interest to us are Ru-C, Ru-N, Ru-O, Ru-P, Ru-S, Ru-Cl, and Ru-H which are common to many of the synthesised ruthenium complexes for various applications as shown in Table 1. The effects of the functional methods and the level of basis sets on the Ru-L bond length and their relative properties are presented with the intention to find cheaper and approachable computational methods for ruthenium complexes.

TABLE 1: The experimental bond distances for Ru-L which are found to be common in different ruthenium complexes.

Ru-C	Ru-N	Ru-O	Ru-P	Ru-S	Ru-Cl	Ru-H
1.827 [44]	1.940 to 2.137 [45]	2.00 to 2.01 [46]	2.2587 to 2.3141 [47]	2.246 to 2.266 [48]	2.2971 to 2.3680 [49]	1.494 [44]
1.845 to 2.220 [50]	2.00 to 2.053 [46]	2.0514 to 2.091 [47]	2.277 [50]	2.2777 to 2.3050 [51]	2.327 to 3.366 [51]	1.57 to 1.59 [52]
1.865 to 2.035 [53]	2.0190 to 2.0914 [49]	2.058 to 2.074 [54]	2.279 to 2.298 [54]	2.3436 to 2.3737 [55]	2.359 to 2.388 [45]	
2.083 [1]	2.024 to 2.114 [51]	2.0656 [51]	2.2812 to 2.4188 [52]		2.3726 to 2.3885 [53]	
2.109 to 2.287 [55]	2.025 to 2.047 [46]	2.066 to 2.092 [44]	2.31 to 2.389 [47]		2.407 to 2.418 [37]	
2.116 to 2.1777 [43]	2.066 to 2.196 [56]	2.076 to 2.109 [49]	2.3165 to 2.3679 [57]		2.407 to 2.4511 [46]	
2.199 to 2.281 [58]	2.0703 to 2.183 [53]	2.0783 to 2.118 [53]	2.336 [46]		2.411 to 2.434 [54]	
	2.0792 [58]	2.18 to 2.23 [59]	2.363 to 2.378 [44]		2.431 to 2.4823 [47]	
	2.107 to 2.122 [60]		2.412 [56]		2.434 to 2.4567 [51]	
	2.141 to 2.196 [44]				2.4357 [1]	

2. Computational Method

Six models of common ruthenium-ligand bonds which are $\text{H}_5\text{Ru-CH}_3$, $\text{H}_5\text{Ru-NH}_2$, $\text{H}_5\text{Ru-OH}$, $\text{H}_5\text{Ru-Cl}$, $\text{H}_5\text{Ru-PH}_3$, and $\text{H}_5\text{Ru-SH}_3$ were built to represent common types of bonds in ruthenium-ligand complexes and in ruthenium-receptor interactions. The models were optimized with DFT hybrid functional like PBE [29] and B3LYP [30] and other higher computational methods like MP2 and CCSD using mixed basis sets of SBKJC VDZ [31] for Ru atom and 6-31+G(d,p) for other atoms. Many of the properties are computed using DGDZVP for Ru, while others were treated with 6-31+G(d,p). Also, for better simulation results, the models were treated with higher perturbation method, MP2, and at higher basis set, aug-cc-pVTZ, for all the atoms including ruthenium. In all the methods, all atoms besides the Ru atom are treated with 6-31+G(d,p) basis set except when basis sets aug-cc-pVTZ was applied on all atoms. Therefore, in the methods where different basis set is applied on Ru atom, the method will be reference based on the type of basis set applied on the Ru atom. All the computational methods, B3LYP/SBKJC-VDZ, PBE/SBKJC-VDZ, MP2/SBKJC-VDZ, CCSD/SBKJC-VDZ, B3LYP/DGDZVP, PBE/DGDZVP, MP2/DGDZVP, and CCSD/DGDZVP, and all other atoms beside Ru atom were treated with 6-31+G(d,p) while in the MP2/aug-cc-pVTZ method, all the atoms were treated with the same basis set. All the computation was done using Gaussian 09 [32] and external basis set aug-cc-pVTZ for Ru atom EMSL Basis Set Library [33, 34] and incorporated into the input file in a format that Gaussian 09 programs can read. The first hyperpolarizability tensors were calculated from the Gaussian output using $(b_{ijk}) = \beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$, where $\beta_x = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})$, $\beta_y = (\beta_{yyy} + \beta_{yxx} + \beta_{yzz})$, and $\beta_z = (\beta_{zzx} + \beta_{zyy} + \beta_{zzz})$ [35, 36]. The atomic units (a.u.) of β in G09 were converted into electrostatic units (esu) ($1 \text{ a.u.} = 8.6393 \times 10^{-33} \text{ esu}$). The IR spectra of the molecules were assigned through the method of potential energy distribution (PED) contributions as implemented in VEDA package [37] and explained in the literatures [38, 39].

3. Results and Discussion

Six models of ruthenium-ligand bonds (Ru-C, Ru-N, Ru-O, Ru-Cl, Ru-P, and Ru-S) are modelled and were optimized using the functionals MP2, CCSD, PBE, and B3LYP. Many of their properties like their hyperpolarizabilities and isotropic and anisotropic shielding tensors are computed using the functionals with different basis sets like SBKJC-VDZ{Ru}6-31+G(d,p), DGDZVP{Ru}6-31+G(d,p), and aug-cc-pVTZ.

3.1. Bonds and the Thermodynamic Properties Dependent on Functional Methods. Different bond distances of ruthenium-ligands (Ru-L) which are reported in the literatures from their crystal structures are shown in Table 1. From the crystal structures of ruthenium complexes, the range of the experimental bond length for Ru-C is 1.827 to 2.281, that of Ru-N is 1.940 to 2.196, that of Ru-O is 2.00 to 2.23, that of Ru-Cl is 2.2971 to 2.4357, that of Ru-P is 2.2587 to 2.412, that of Ru-S is 2.246 to 2.3737, and that of Ru-H is 1.494 to 1.59 (Table 1). The general features of the experimental Ru-L bond lengths are in the order of Ru-Cl > Ru-P > Ru-S > Ru-O > Ru-N > Ru-C > Ru-H. The Ru-L bond distances of the six models which are obtained from the optimized geometries at MP2, CCSD, PBE, and B3LYP level of theories are shown in Figure 1. The general features of the Ru-L bond lengths of the six models using different computational methods show a common order of Ru-P > Ru-S > Ru-Cl > Ru-C > Ru-O > Ru-N. The observed similarity in the bond orders between the experimental and theoretical is that they both rated Ru-Cl, Ru-P, and Ru-S higher than Ru-O, Ru-N, and Ru-C. The computed range of bond values for Ru-C is 1.94 to 1.98 in the order of MP2 < PBE < B3LYP < CCSD, that of Ru-N is 1.83 to 1.87 in the order of MP2 < B3LYP < CCSD < PBE, that of Ru-O is 1.85 to 1.87 in the order of MP2 < CCSD < B3LYP < PBE, that of Ru-Cl is 2.17 to 2.21 in the order of MP2 < CCSD < B3LYP < PBE, that of Ru-P is 2.39 to 2.45 in the order of MP2 < PBE < B3LYP < CCSD, and that of Ru-S is 2.21 to 2.24 in the order of MP2 < PBE < B3LYP < CCSD. In both Ru-N and Ru-Cl, the functional PBE overestimates the bonds

FIGURE 1: The bond distances of the six models of Ru-L bonds obtained from the optimized geometries at MP2, CCSD, PBE, and B3LYP using SBKJC VDZ basis set.

TABLE 2: The bond distances and thermodynamic properties using MP2/ECP method and the differences using other methods (energies in KJ/Mol).

Method/bonds	Distance	Energy	Zero energy	Thermal energy	Enthalpy	Gibbs-free	CV KJ/Mol-K	S KJ/Mol-K
Ru-C-MP2-ECP	1.9485	$-3.5376E+05$	$-3.5457E+05$	$-3.5455E+05$	$-3.5455E+05$	$-3.5464E+05$	0.0782	0.2901
Ru-N-MP2-ECP	1.8342	$-3.5376E+05$	$-3.5457E+05$	$-3.5455E+05$	$-3.5455E+05$	$-3.5464E+05$	0.0782	0.2901
Ru-O-MP2-ECP	1.8501	$-3.9584E+05$	$-3.9681E+05$	$-3.9679E+05$	$-3.9679E+05$	$-3.9688E+05$	0.0769	0.2940
Ru-Cl-MP2-ECP	2.1711	$-4.4927E+05$	$-4.5022E+05$	$-4.5021E+05$	$-4.5021E+05$	$-4.5029E+05$	0.0736	0.2927
Ru-P-MP2-ECP	2.3969	$-1.1493E+06$	$-1.1499E+06$	$-1.1499E+06$	$-1.1499E+06$	$-1.1500E+06$	0.0973	0.3293
Ru-S-MP2-ECP	2.2157	$-1.2964E+06$	$-1.2973E+06$	$-1.2972E+06$	$-1.2972E+06$	$-1.2973E+06$	0.0855	0.3188
Difference of the other methods from MP2/SBKJC VDZ								
Ru-C-PBE-ECP	0.0024	$-2.9890E+03$	$-1.9950E+03$	$-1.9946E+03$	$-1.9946E+03$	$-1.9955E+03$	0.0017	0.0032
Ru-N-PBE-ECP	0.0120	$-2.9890E+03$	$-1.9950E+03$	$-1.9946E+03$	$-1.9946E+03$	$-1.9955E+03$	0.0017	0.0032
Ru-O-PBE-ECP	0.0243	$-3.1318E+03$	$-1.9966E+03$	$-1.9970E+03$	$-1.9970E+03$	$-1.9959E+03$	-0.0011	-0.0037
Ru-Cl-PBE-ECP	0.3088	$-3.2116E+03$	$-2.1228E+03$	$-2.1223E+03$	$-2.1223E+03$	$-2.1231E+03$	0.0021	0.0027
Ru-P-PBE-ECP	0.0219	$-3.5356E+03$	$-2.7378E+03$	$-2.7373E+03$	$-2.7373E+03$	$-2.7386E+03$	0.0009	0.0043
Ru-S-PBE-ECP	0.0074	$-3.7839E+03$	$-2.8207E+03$	$-2.8208E+03$	$-2.8208E+03$	$-2.8202E+03$	0.0007	-0.0019
Ru-C-B3LYP-ECP	0.0159	$-3.1831E+03$	$-2.1836E+03$	$-2.1828E+03$	$-2.1828E+03$	$-2.1844E+03$	0.0039	0.0055
Ru-N-B3LYP-ECP	0.0047	$-4.5407E+04$	$-4.4429E+04$	$-4.4429E+04$	$-4.4429E+04$	$-4.4429E+04$	-0.0012	0.0010
Ru-O-B3LYP-ECP	0.0144	$-3.3288E+03$	$-2.1890E+03$	$-2.1893E+03$	$-2.1893E+03$	$-2.1884E+03$	0.0000	-0.0028
Ru-Cl-B3LYP-ECP	0.0392	$-3.4479E+03$	$-2.3536E+03$	$-2.3531E+03$	$-2.3531E+03$	$-2.3540E+03$	0.0022	0.0031
Ru-P-B3LYP-ECP	0.0398	$-4.0797E+03$	$-3.2774E+03$	$-3.2764E+03$	$-3.2764E+03$	$-3.2788E+03$	0.0031	0.0081
Ru-S-B3LYP-ECP	0.0125	$-4.3126E+03$	$-3.3423E+03$	$-3.3431E+03$	$-3.3431E+03$	$-3.3414E+03$	-0.0029	-0.0057
Ru-C-CCSD-ECP	0.0316	$-2.1515E+01$	$-7.1138E+01$	$-6.9570E+01$	$-6.9570E+01$	$-7.2697E+01$	0.0075	0.0105
Ru-N-CCSD-ECP	0.0436	$-4.2095E+04$	$-4.2295E+04$	$-4.2294E+04$	$-4.2294E+04$	$-4.2295E+04$	0.0024	0.0047
Ru-O-CCSD-ECP	0.0109	$-1.6767E+01$	$-5.4986E+01$	$-5.4600E+01$	$-5.4600E+01$	$-5.4878E+01$	0.0037	0.0009
Ru-Cl-CCSD-ECP	0.0368	$-2.4604E+01$	$-6.5007E+01$	$-6.4330E+01$	$-6.4330E+01$	$-6.5559E+01$	0.0037	0.0041
Ru-P-CCSD-ECP	0.0512	$-1.4740E+00$	$-1.2560E+02$	$-1.2351E+02$	$-1.2351E+02$	$-1.2915E+02$	0.0066	0.0189
Ru-S-CCSD-ECP	0.0211	$-3.7429E+01$	$-9.8966E+01$	$-9.9562E+01$	$-9.9562E+01$	$-9.8230E+01$	-0.0017	-0.0045

above other functional methods. Ru-C bond values of our model are within the common experimental bond values for Ru-C, while the values obtained for other modelled bonds are little below the common experimental values. If the bond values obtained using the MP2 are compared to the analytical values, the differences in the values of other computational

methods from MP2 are calculated using simple expression $X_{\text{other}} - X_{\text{MP2}}$ and are presented in Table 2. The differences in bond values obtained using PBE compared to the analytical values from MP2 are smaller in magnitude compared to other methods (Table 2) but the order of the bond distances in the model was not perfectly reproduced as in B3LYP and CCSD

FIGURE 2: The superposition of different model of Ru-L bonds obtained using MP2 (green), CCSD (blue), PBE (yellow), and B3LYP (cyan) to determine the RMSD of the whole geometries after the optimization of their respective geometries.

TABLE 3: The correlation of the values of energy and thermodynamics properties at MP2/SBKJC VDZ with other computational methods.

MP2-ECP	PBE	B3LYP	CCSD
Ru-L-dist	1.00	1.00	1.00
Energy	1.00	1.00	1.00
Zero energy	1.00	1.00	1.00
Thermal energy	1.00	1.00	1.00
Enthalpy	1.00	1.00	1.00
Gibbs-free	1.00	1.00	1.00
CV	0.99	0.97	0.95
Entropy	0.98	0.95	0.92

(Table 3). All the thermodynamic properties were computed at 298.150 Kelvin and pressure 1 Atm. The magnitude of the differences in thermodynamic properties (Table 2) shows that CCSD and PBE give closer values to MP2 than B3LYP. Also, considering the reproducibility of the order of bond distances obtained from MP2 in the other methods, all the computational methods produced a perfect order for the thermodynamic energies except PBE which gave a relatively better order for the CV and the entropy (Table 3). This is an indication that PBE performs better for geometrical optimization and computation of thermodynamic properties which agree well with the literatures that reported PBE correlation in combination with SBKJC VDZ ECP basis set as a good method for the optimization of metal complexes [40, 41]. The computed types of energies using other methods of computation are higher in negative values than MP2, while their bond distance, CV, and S are higher in positive values. Considering the RMSD of all the atoms in each of the models as shown in Table 4 and Figure 2, the optimized geometries obtained for the models Ru-C, Ru-O, and Ru-S at various computational methods are very similar to lower RMSD compared to what was obtained for the models Ru-N, Ru-Cl, and Ru-P. Also, the RMSD of the optimized geometries obtained from the functional PBE are lower than those

TABLE 4: The RMSD of the optimized geometries obtained from other methods of computation from that obtained from MP2 using SBKJC VDZ ECP basis set.

	B3LYP	CCSD	PBE
Ru-C	0.963	1.347	0.637
Ru-N	1.030	1.032	1.035
Ru-O	0.056	0.072	0.065
Ru-Cl	1.302	1.030	1.268
Ru-P	1.203	1.221	1.190
Ru-S	0.265	0.266	0.252

obtained from B3LYP and CCSD which further supports PBE as a good method for the optimization of ruthenium complexes.

3.2. Energy, HOMO, LUMO, Shielding Tensors, and J-Coupling. The values of the energy, HOMO, LUMO, and isotropic and anisotropic shielding computed at MP2/aug-cc-pVTZ and the variations obtained when computed with other methods are presented in Table 5. The shielding tensors were computed using Gauge-Independent Atomic Orbital (GIAO) method. The values of the energy and the variation obtained at different functional and basis sets show that variation in the energy values using different functional is lower compared to variation in the energy values using different basis sets. This is an indication that the energy values depend more on the type of basis sets rather than on the type of the functional. However, the variation in the values of HOMO, LUMO, and isotropic and anisotropic shielding at different functional methods shows that they depend more on the type of the functional and the geometrical change rather than on the type of the basis sets. The difference in the values of HOMO, LUMO, and isotropic and anisotropic shielding within MP2 methods at different basis set is lower compared to changing the functional to PBE and B3LYP. Also, B3LYP seems to perform better than PBE as the differences obtained at B3LYP are far lower compared to PBE. Also, considering the reproducibility of the order of these properties at different

TABLE 5: The energy, shielding tensors, and J -coupling values using MP2/acc method and the differences using other computational methods (the energy values in Hartree).

	Energy	HOMO	LUMO	Ru-Iso	Ru-Aniso	X-Iso	X-Aniso
Ru-C-MP2-acc	-4403.52	-0.92	-0.42	-7421.80	10691.11	-149.88	522.69
Ru-N-MP2-acc	-4418.77	-0.90	-0.46	-11760.15	9465.97	-825.79	1788.60
Ru-O-MP2-acc	-4439.24	-0.68	-0.18	-9188.58	8466.75	-166.94	1194.28
Ru-Cl-MP2-acc	-4823.19	-0.62	-0.20	-11224.11	10522.28	298.22	2384.76
Ru-P-MP2-acc	-4705.44	-0.87	-0.37	-13590.81	14885.90	448.61	41.41
Ru-S-MP2-acc	-4763.85	-0.61	-0.16	-3133.38	5826.99	-804.39	2375.77
			0.00				
Ru-C-MP2-dv	-78.49	0.00	0.00	261.83	-389.01	11.48	6.59
Ru-N-MP2-dv	-79.26	0.00	-0.01	710.88	-701.10	33.43	-13.44
Ru-O-MP2-dv	-79.14	0.00	0.00	-446.94	-395.12	-137.68	243.27
Ru-Cl-MP2-dv	-79.24	0.00	0.00	-372.54	1144.75	-197.16	354.79
Ru-P-MP2-dv	-79.57	0.00	0.00	-1779.17	2465.57	25.18	-0.37
Ru-S-MP2-dv	-77.19	0.02	-0.02	-6116.50	1355.58	-205.80	358.51
Ru-C-MP2-ECP	4268.78	0.00	-0.01	5965.28	-9200.85	13.11	1.93
Ru-N-MP2- ECP	4268.00	0.00	0.00	9603.19	-8131.49	74.35	-74.55
Ru-O-MP2- ECP	4268.12	0.00	0.00	7403.24	-7159.56	-82.99	156.74
Ru-Cl-MP2- ECP	4268.02	0.00	0.00	9144.27	-8674.35	-164.84	411.30
Ru-P-MP2- ECP	4267.70	0.00	-0.01	10936.80	-12181.57	32.60	-13.17
Ru-S-MP2- ECP	4270.07	0.03	-0.03	1497.43	-4965.80	137.97	-144.94
Ru-C-PBE-dv	-80.75	0.20	-0.22	-51.06	-7670.06	349.29	-461.55
Ru-N-PBE-dv	-81.56	0.18	-0.20	6292.61	-4964.09	526.42	-926.41
Ru-O-PBE-dv	-81.47	0.22	-0.18	138164.39	159842.43	-3839.42	4139.74
Ru-Cl-PBE-dv	-81.76	0.15	-0.18	103219.55	132875.50	-4910.03	43707.95
Ru-P-PBE-dv	-82.01	0.21	-0.21	165474.51	373242.21	3740.88	14462.38
Ru-S-PBE-dv	-79.73	0.18	-0.19	106543.31	103474.55	-6590.68	12307.39
Ru-C-PBE-ECP	4267.64	0.21	-0.21	6637.60	-10275.35	75.97	-170.75
Ru-N-PBE-ECP	4266.81	0.18	-0.20	10714.04	-8849.98	530.35	-933.20
Ru-O-PBE-ECP	4266.90	0.22	-0.18	-33810.33	382779.43	-30918.12	350412.47
Ru-Cl-PBE-ECP	4266.60	0.15	-0.18	-7575.42	25794.02	271608.96	
Ru-P-PBE-ECP	4266.35	0.21	-0.21	191099.00	962614.33		
Ru-S-PBE-ECP	4268.63	0.18	-0.19	95225.96	321193.44	115652.09	358353.34
Ru-C-B3LYP-dv	-81.28	0.16	-0.18	812.27	-5887.37	48.60	-120.06
Ru-N-B3LYP-dv	-82.11	0.13	-0.17	4319.91	-2755.91	451.12	-755.40
Ru-O-B3LYP-dv	-82.03	0.17	-0.16	2733.24	-3813.98	-233.91	68.13
Ru-Cl-B3LYP-dv	-82.46	0.12	-0.16	2548.50	-2846.75	-2658.07	3095.48
Ru-P-B3LYP-dv	-82.70	0.16	-0.19	4725.61	-6464.13	-54.51	91.37
Ru-S-B3LYP-dv	-80.41	0.14	-0.17	-2259.01	-2504.44	307.08	-722.43
Ru-C-B3LYP-ECP	4267.57	0.16	-0.18	6249.66	-10039.53	49.04	-123.01
Ru-N-B3LYP-ECP	4266.73	0.13	-0.17	10402.50	-8531.88	459.60	-771.45
Ru-O-B3LYP-ECP	4266.81	0.17	-0.16	8020.53	-7805.23	-197.73	-2.44
Ru-Cl-B3LYP-ECP	4266.38	0.12	-0.16	9776.24	-9480.89	-2364.64	2645.00
Ru-P-B3LYP-ECP	4266.14	0.16	-0.18	12079.02	-13760.28	-48.06	79.68
Ru-S-B3LYP-ECP	4268.43	0.14	-0.17	2124.24	-5365.94	332.76	-746.43

MP2-acc stands for MP2/aug-cc-pVTZ, MP2-dv stands for MP2/DGDZVP, MP2-ECP stands for MP2/SBKJC VDZ, PBE-dv stands for PBE/DGDZVP, PBE-ECP stands for PBE/SBKJC VDZ, B3LYP-dv stands for B3LYP/DGDZVP, and B3LYP-ECP stands for B3LYP/SBKJC VDZ.

TABLE 6: Correlation of other methods of computation with the MP2/acc in computing energy, HOMO, LUMO, and isotropic and anisotropic shielding.

	MP2/DGDZVP	MP2/SBKJC VDZ	PBE/DGDZVP	PBE/SBKJC VDZ	B3LYP/DGDZVP	B3LYP/SBKJC VDZ
Energy	1.00	1.00	1.00	1.00	1.00	1.00
HOMO	1.00	1.00	0.99	0.99	0.99	0.99
LUMO	1.00	1.00	1.00	0.99	1.00	1.00
Ru-Iso	0.74	0.83	-0.09	-0.11	0.91	0.94
Ru-Aniso	0.95	0.97	0.51	0.50	0.84	0.82
X-Iso	0.98	0.98	0.67	-0.51	-0.16	-0.12
X-Aniso	0.99	0.98	-0.35	0.33	0.71	0.73

TABLE 7: J -coupling of the Ru-L bonds at different level of computational methods.

	PBE/DGDZVP	PBE/SBKJC VDZ	B3LYP/DGDZVP	B3LYP/SBKJC VDZ
Ru-C	$-1.85E + 001$	$1.14E + 000$	$-2.68E + 000$	$1.36E + 000$
Ru-N	$-1.46E + 001$	$7.53E - 001$	$6.56E + 001$	$6.07E + 000$
Ru-O	$2.45E + 001$	$-9.80E - 001$	$2.49E + 001$	$-1.17E + 000$
Ru-Cl	$4.72E + 001$	$5.63E + 000$	$4.76E + 001$	$5.90E + 000$
Ru-P	$-6.51E + 001$	$-3.14E - 001$	$-7.14E + 001$	$-5.00E - 001$
Ru-S	$-7.52E - 001$	$1.06E + 000$	$4.69E - 001$	$1.35E + 000$

TABLE 8: Correlation of J -coupling within the methods.

	PBE/DGDZVP	PBE/SBKJC VDZ	B3LYP/DGDZVP	B3LYP/SBKJC VDZ
PBE-dv	1.00	0.58	0.74	0.37
PBE-ECP	0.58	1.00	0.42	0.73
B3LYP-dv	0.74	0.42	1.00	0.72
B3LYP-ECP	0.37	0.73	0.72	1.00

computational methods (Table 6), only the energy order is perfectly reproduced by all the methods. There is a very high similarity in the order of HOMO and LUMO, especially LUMO computed using B3LYP. In addition, B3LYP is found to also perform better in reproducing the shielding tensors of Ru and other atoms compared to PBE except for the order of the isotropic shielding of other atoms besides Ru atom. The correlation obtained from B3LYP in computing shielding tensors further supports its reported better performance for these properties [42].

In computation of the J -coupling, we are only limited to B3LYP and PBE since these properties are not permitted in Gaussian package at MP2 and CCSD level of computation. Considering the magnitude of J -coupling at B3LYP/DGDZVP, it follows the order Ru-P > Ru-N > Ru-Cl > Ru-S > Ru-O > Ru-C (Table 7). The order is well reproduced in B3LYP with ECP basis set but is poor in PBE and is even the worst when PBE is combined with ECP basis set (Table 8). The simple reason for the variations is in support of the literature report demonstrating that the J -coupling is sensitive to bonding interactions [43].

3.3. Hyperpolarizability Properties. The values of the computed hyperpolarizabilities of the six models using different functionals and basis sets are shown in Table 9. The values of the hyperpolarizabilities of the models using MP2 functionals at different basis sets are in the order of Ru-S > Ru-O > Ru-Cl > Ru-N > Ru-P > Ru-C which suggest the level of their possible modelling for NLO application. The order obtained

from CCSD is Ru-O > Ru-Cl > Ru-S > Ru-P > Ru-N > Ru-C; the PBE methods give the order Ru-Cl > Ru-C < Ru-S > Ru-O > Ru-P > Ru-N and B3LYP gives the order Ru-Cl > Ru-O > Ru-S > Ru-P > Ru-N > Ru-C. The MP2 rated Ru-S as the best model for NLO application, while CCSD rated model Ru-O as the best. Also, a different model, Ru-Cl, is indicated to have the highest hyperpolarizabilities using the functionals PBE and B3LYP irrespective of the basis set used. The correlations of the hyperpolarizabilities values among the models are shown in Table 10. The correlation table shows that the order of the hyperpolarizabilities of the models is perfectly reproducible using the same MP2 at different basis sets and also within CCSD at different basis sets. Also, B3LYP performs better in reproducing its order at different basis set compared to PBE. This clearly shows that the order of the hyperpolarizabilities depends greatly on the geometrical configuration and the type of the functional used rather than on the type of the basis sets. The only observed similarity in the order of the hyperpolarizabilities computed with different methods is that all the methods rated the models Ru-S, Ru-Cl, and Ru-O among the best three except for PBE which excluded Ru-O from its best three.

3.4. The IR Vibrations. The IR vibrations of the models at different computational methods are shown in Figure 3. The vibrations which are of significant interest to us are their Ru-ligand bonds of Ru-C, Ru-N, Ru-O, Ru-Cl, Ru-P, and Ru-S which are shown in Table 11. Also, most of the prominent vibrations are assigned as shown in Table 12. In

TABLE 9: The first hyperpolarizability (β) in esu (1×10^{-30}) values at different computational methods.

	MP2/aug-cc-pVTZ	MP2/DGDZVP	MP2/SBKJC VDZ	CCSD/DGDZVP	CCSD/SBKJC VDZ	PBE/DGDZVP	PBE/SBKJC VDZ	B3LYP/DGDZVP	B3LYP/SBKJC VDZ
Ru-C	1.53	1.79	1.71	1.08	0.98	2.44	0.28	0.55	0.55
Ru-N	5.69	2.24	3.80	1.05	1.09	0.77	0.63	0.76	0.62
Ru-O	35.05	17.91	18.60	8.22	5.48	1.78	1.60	2.20	2.05
Ru-Cl	11.73	14.40	13.25	5.58	5.47	2.84	2.89	3.25	3.13
Ru-P	1.77	1.80	2.13	1.24	1.51	1.52	1.47	1.35	1.37
Ru-S	282.14	335.91	1147.78	2.95	3.15	2.14	1.82	2.07	1.65

TABLE 10: The correlation within the different methods used in computing the first hyperpolarizabilities.

	MP2/aug-cc-pV'TZ	MP2/DGDZVP	MP2/SBKJC VDZ	CCSD/DGDZVP	CCSD/SBKJC VDZ	PBE/DGDZVP	PBE/SBKJC VDZ	B3LYP/DGDZVP	B3LYP/SBKJC VDZ
MP2-acc	1.00	1.00	1.00	0.04	0.14	0.19	0.30	0.24	0.10
MP2-dv	1.00	1.00	1.00	-0.01	0.10	0.20	0.29	0.22	0.09
MP2-ecp	1.00	1.00	1.00	-0.05	0.06	0.19	0.27	0.19	0.06
CCSD-dv	0.04	-0.01	-0.05	1.00	0.95	0.31	0.62	0.75	0.75
CCSD-ECP	0.14	0.10	0.06	0.95	1.00	0.45	0.81	0.92	0.91
PBE-dv	0.19	0.20	0.19	0.31	0.45	1.00	0.42	0.51	0.53
PBE-ECP	0.30	0.29	0.27	0.62	0.81	0.42	1.00	0.97	0.95
B3LYP-dv	0.24	0.22	0.19	0.75	0.92	0.51	0.97	1.00	0.99
B3LYP-ECP	0.10	0.09	0.06	0.75	0.91	0.53	0.95	0.99	1.00

FIGURE 3: The IR vibrations of the six models computed using MP2 (black), CCSD (red), PBE (green), and B3LYP (blue).

TABLE 11: The IR vibrations of the Ru-L bonds at different computational methods.

	B3LYP			CCSD			MP2			PBE		
Ru-C	607.77	23.49	$\beta(\text{HRuH}), \nu(\text{Ru-C})$	587.27	33.46	$\nu(\text{Ru-C})$	682.24	1.95	$\nu(\text{Ru-C})$	632.97	22.6	$\beta(\text{HRuH}), \nu(\text{Ru-C})$
	502.22	2.38	$\tau(\text{HRuCH}), \nu(\text{Ru-C})$							530.62	71	$\beta(\text{HRuH}), \nu(\text{Ru-C})$
Ru-N	718.99	9.77	$\nu(\text{Ru-N}), \nu(\text{Ru-H})$	623.52	16.36	$\nu(\text{Ru-N})$	662.65	28.79	$\beta(\text{HRuH}), \nu(\text{Ru-N})$	714.95	10.13	$\nu(\text{Ru-N})$
Ru-O	717.81	13.71	$\nu(\text{Ru-O})$	482.35	1.01	$\nu(\text{Ru-N})$	495.39	7.38	$\nu(\text{Ru-N})$	656.08	13.7	$\beta(\text{HRuH}), \nu(\text{Ru-N})$
				634.12	15.86	$\nu(\text{Ru-O})$	705.74	7.5	$\nu(\text{Ru-O})$	688.89	23.95	$\nu(\text{Ru-O})$
Ru-Cl	435.29	21.95	$\nu(\text{Ru-Cl})$	591.33	6.44	$\nu(\text{Ru-Cl})$	657.32	37.6	$\nu(\text{Ru-Cl})$	323.31	10.22	$\nu(\text{Ru-Cl})$
				447.84	34.33	$\nu(\text{Ru-Cl})$						
Ru-P	282.03	1.71	$\nu(\text{Ru-P})$	239.39	3.95	$\nu(\text{Ru-P})$	445.35	2.32	$\nu(\text{Ru-P})$	279.37	10.25	$\sigma(\text{RuHPh}), \nu(\text{Ru-P})$
										234.42	7.11	$\sigma(\text{RuHPh}), \nu(\text{Ru-P})$
Ru-S	411.94	4.01	$\nu(\text{Ru-S})$							408.66	3.11	$\nu(\text{Ru-S})$
	373.11	5.97	$\sigma(\text{RuHSH}), \nu(\text{Ru-S})$	326.19	4.24	$\nu(\text{Ru-S})$	357.49	24.96	$\sigma(\text{RuHSH}), \nu(\text{Ru-S})$	385.96	19.99	$\nu(\text{Ru-S})$

ν is stretching, β is bending, τ is torsional, and σ is out-of-plane torsional.

TABLE 12: The assignment of the prominent IR vibrations of the models at different computational methods.

	B3LYP			CCSD			MP2			PBE		
Ru-C	3467.83	96.24	$\beta(\text{HRuH}), \nu(\text{Ru-H})$	3866.28	124	$\beta(\text{HRuH}), \beta(\text{HRuH}), \nu(\text{CH}), \nu(\text{Ru-H})$	3817.59	151.01	$\beta(\text{HRuH}), \beta(\text{HRuH}), \tau(\text{HRuHC}), \nu(\text{CH}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$	3051.1	103	$\nu(\text{CH}), \nu(\text{HRuH}), \nu(\text{CH}), \nu(\text{RuHCH}), \nu(\text{CH}), \nu(\text{RuHCH}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$
	3132.41	87.72	$\nu(\text{CH}), \nu(\text{CH})$	3445.85	60.03	$\nu(\text{Ru-H})$	3265.34	58.2	$\beta(\text{HCH}), \nu(\text{CH}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$	3044.61	51.91	$\nu(\text{CH}), \nu(\text{RuHCH}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$
	3065.01	56.14	$\beta(\text{HRuH}), \beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	3237.18	74.02	$\beta(\text{HCH}), \beta(\text{HRuH}), \nu(\text{CH}), \nu(\text{CH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	3105.76	79.13	$\beta(\text{HRuH}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$	2910.41	166.77	$\nu(\text{CH}), \nu(\text{CH})$
	2998.73	143.81	$\nu(\text{CH}), \nu(\text{CH})$	3106.07	104.81	$\beta(\text{HRuH}), \tau(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2309.69	68.51	$\beta(\text{HRuH}), \tau(\text{HRuH}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$	2471.28	44.98	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$
	2400.85	109.51	$\nu(\text{CH})$	2319.44	101.47	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2075.53	96.9	$\beta(\text{HRuH}), \beta(\text{HRuH}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$	2323.14	129.68	$\nu(\text{CH})$
Ru-N	3802.07	142.05	$\beta(\text{HRuH}), \beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	4010.43	123.1	$\beta(\text{HRuH}), \tau(\text{HRuH}), \nu(\text{NH}), \nu(\text{NH})$	4034.78	114.28	$\tau(\text{HRuH}), \nu(\text{NH}), \nu(\text{NH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	3532.89	106.73	$\beta(\text{HRuH}), \beta(\text{HRuH}), \nu(\text{NH}), \nu(\text{NH})$
	3390.19	200.19	$\nu(\text{NH}), \nu(\text{NH})$	3478.97	181.19	$\beta(\text{HRuH}), \beta(\text{HRuH}), \tau(\text{HRuH}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$	3474.97	186.6	$\beta(\text{HRuH}), \beta(\text{HRuH}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$	3315.04	192.82	$\nu(\text{NH}), \nu(\text{NH})$
	3268.71	398.39	$\nu(\text{NH}), \nu(\text{NH})$	3367.28	289.75	$\nu(\text{Ru-H}), \nu(\text{Ru-H})$	3326.95	149.95	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	3183.72	375.24	$\nu(\text{NH}), \nu(\text{NH})$
	2931.51	42.14	$\nu(\text{Ru-H}), \nu(\text{Ru-H}), \nu(\text{NH}), \nu(\text{NH})$	3270.85	35.14	$\beta(\text{HRuH}), \tau(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2746.17	45.5	$\nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2389.61	40.07	$\beta(\text{HRuH}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$
	2079.16	61.08	$\nu(\text{Ru-H})$	1999.79	43.38	$\beta(\text{HCH}), \nu(\text{HCH})$	2105.24	64.43	$\nu(\text{HCH}), \nu(\text{HCH}), \nu(\text{HCH}), \nu(\text{HCH})$	2037.34	65.57	$\nu(\text{Ru-H})$
Ru-O	3726.13	269.49	$\nu(\text{OH})$	3807.49	280.41	$\nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	3890.61	10.05	$\nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	3608.77	239.93	$\nu(\text{OH})$
	2759.32	14.07	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	3107.9	19.21	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	3709.79	518.91	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	3279.56	29.92	$\beta(\text{HRuH}), \beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$
	1859.8	23.33	$\nu(\text{Ru-H}), \nu(\text{Ru-H})$	1794.43	23.74	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2915.06	550.2	$\nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2200.79	15.99	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$
	1346.08	28.94	$\nu(\text{Ru-H}), \nu(\text{Ru-H})$	1256.32	28.95	$\nu(\text{Ru-H}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2604.61	45.69	$\nu(\text{OH}), \beta(\text{HORu}), \nu(\text{OH}), \beta(\text{HORu})$	2030.14	15.88	$\nu(\text{Ru-H})$
	1127.41	94.79	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	1092.35	73.74	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2051.06	33.83	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	1479.34	29	$\nu(\text{Ru-H}), \nu(\text{Ru-H}), \nu(\text{Ru-H})$
Ru-Cl	1855.46	24.58	$\nu(\text{Ru-H})$	3086.67	14.11	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	3036.51	236.53	$\nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2208.8	22.42	$\nu(\text{Ru-H})$
	1317.51	32.88	$\nu(\text{Ru-H})$	1799.47	25.11	$\nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2611.79	30.15	$\nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2108.16	11.24	$\nu(\text{Ru-H})$
	1145.81	94.21	$\nu(\text{Ru-H})$	1211.59	32.69	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2039.9	30.06	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	2031.12	16.87	$\nu(\text{Ru-H})$
	847.59	31.57	$\nu(\text{Ru-H})$	1108.61	72.22	$\nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	1312.24	35.65	$\nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	1472.93	31.51	$\nu(\text{Ru-H})$
	794.88	38.1	$\beta(\text{HRuH})$	768.7	24.83	$\beta(\text{HRuH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	1091.64	150.1	$\nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH}), \nu(\text{RuHCH})$	113.46	919.53	$\beta(\text{HRuH})$

TABLE 12: Continued.

	B3LYP			CCSD			MP2			PBE		
	3845.75	154.7	$\beta(\text{HRuH})$	4085.67	162.07	$\beta(\text{HRuH}), \tau(\text{HRuPH}),$ $\sigma(\text{RuHPH}),$	4101.48	113.61	$\beta(\text{HRuH}), \beta(\text{HRuH})$	3509.87	96.45	$\beta(\text{HRuH}), \nu(\text{Ru-H})$
	2963.63	14.57	$\beta(\text{HRuH}), \nu(\text{Ru-H})$	3282.27	15.08	$\beta(\text{HRuH}), \beta(\text{HRuH}),$ $\tau(\text{HPRuH}),$	2649.75	42.73	$\beta(\text{HRuP}), \nu(\text{Ru-H})$	2462.59	48.71	$\nu(\text{PH}), \nu(\text{PH})$
Ru-P	2536.28	40.06	$\nu(\text{PH}), \nu(\text{PH})$	2617.21	31.38	$\nu(\text{Ru-H})$	2623.36	47.52	$\beta(\text{HRuH}), \tau(\text{HRuPH}),$ $\nu(\text{Ru-H}),$	2430.7	56.89	$\nu(\text{PH}), \nu(\text{PH})$
	2506.03	46.24	$\nu(\text{PH}), \nu(\text{PH})$	2593.79	35.79	$\beta(\text{HRuP})$	2569.33	48.65	$\beta(\text{HRuP}), \beta(\text{HRuH})$	2384.68	13.06	$\beta(\text{HRuH}), \tau(\text{HRuPH}),$ $\nu(\text{Ru-H}),$
	2458.99	70.96	$\nu(\text{PH}), \nu(\text{PH})$	2554.19	44.27	$\beta(\text{HRuH}), \tau(\text{HPRuH}),$ $\tau(\text{HPRuH}),$	2286.33	86.92	$\beta(\text{HRuH}), \nu(\text{PH})$	2373.54	92	$\nu(\text{PH})$
	2650.41	13.08	$\nu(\text{SH})$	2907.93	37.8	$\beta(\text{HRuH}), \tau(\text{HSRuH}),$ $\nu(\text{Ru-H}), \beta(\text{HRuS})$	4171.99	154.87	$\sigma(\text{RuHSH}), \sigma(\text{RuHSH}),$ $\beta(\text{HRuH}),$	3460.6	23.84	$\beta(\text{HRuH}), \beta(\text{HRuH}),$ $\beta(\text{HRuH}), \sigma(\text{RuHSH})$
	2634.2	19.16	$\beta(\text{HRuH}), \nu(\text{Ru-H})$	1880.73	16.85	$\beta(\text{HRuH}), \beta(\text{HRuH}),$ $\nu(\text{Ru-H}),$	2804.1	1992.65	$\beta(\text{HRuS}), \beta(\text{HRuH}),$ $\beta(\text{HRuH}), \nu(\text{Ru-H})$	2582.25	12.54	$\nu(\text{SH})$
Ru-S	1913	16.99	$\nu(\text{Ru-H})$	1148.53	29.67	$\tau(\text{HSRuH}), \nu(\text{SH}),$ $\nu(\text{Ru-H}),$	2385.44	23923.74	$\beta(\text{HRuS})$	2167.5	26.04	$\nu(\text{Ru-H})$
	1216.42	33.86	$\nu(\text{Ru-H}), \nu(\text{Ru-H})$	1098.59	101.32	$\beta(\text{HRuH}), \tau(\text{HSRuH}),$ $\sigma(\text{RuHSH}), \nu(\text{Ru-H})$	2257.61	448.94	$\nu(\text{Ru-H}), \beta(\text{HRuH})$	1320.47	36.99	$\nu(\text{Ru-H}), \nu(\text{Ru-H})$
	1108.6	110.06	$\beta(\text{HRuH}), \nu(\text{Ru-H})$	825.34	33.1	$\tau(\text{HSRuH}), \nu(\text{Ru-H}),$ $\nu(\text{Ru-H}),$	2106.43	52.05	$\nu(\text{Ru-H})$	883.5	50.98	$\sigma(\text{RuHSH}), \sigma(\text{RuHSH}),$ $\nu(\text{Ru-H}), \nu(\text{Ru-H})$

all the methods, Ru-C, Ru-N, and Ru-O vibrations are within the range of 500 to 720 which is far higher than the range of vibrations of Ru-Cl, Ru-P, and Ru-S which are found within the range of 224 to 658. Generally, the order of Ru-L vibrations can be assumed as Ru-N > Ru-O > Ru-C > Ru-Cl > Ru-S > Ru-P (Table 11). The wavenumbers of the vibrations computed from the different methods appear to be significantly different from each other in values and positions (Figure 3). The features of the IR spectra using MP2 and CCSD are very similar in the models. Some vibration around 2915.06 in model Ru-O, 3036.51 in Ru-Cl, and 2385.44 in Ru-S are very prominent in MP2 methods compared to in any other methods or even absent in other methods. For instance, the bending of the angle of HRuS which is found to be prominent in MP2 method is completely absent in other methods (see Figure 3 and Table 12). The MP2 and CCSD show strong vibrations within the range of 3800 to 4100 in many of the models which are obviously absent in many of the PBE and B3LYP methods. Using the PED method as implemented in VEDA package, most of these vibrations at high frequencies are a result of the torsional and out-of-plane vibration of H-Ru-X-H, where X represents the type of the model as shown in Table 12. In addition, most of the bending vibrations which are determined by PBE and B3LYP from 2800 to 3800 in the models are also determined by MP2 and CCSD, though some cases are at lower wavenumber compared to PBE and B3LYP (Table 12). In the models Ru-O and Ru-Cl, PBE and B3LYP give priority to the OH and RuH vibrations, respectively, while MP2 and CCSD give priority to the torsional stretching and angle bending of their atoms.

4. Conclusions

Six models of Ru-L bonds, Ru-C, Ru-N, Ru-O, Ru-Cl, Ru-P, and Ru-S, are built to represent common ruthenium complexes and possible ruthenium-receptor interactions. The reproducibility of their geometrical, electronic, spectroscopic, and conductive properties was investigated using MP2, CCSD, PBE, and B3LYP functionals with different combination of basis sets. Generally, we observed that the reproducibility of most of the properties is much easier using different basis sets compared to using different functional methods as a result of significant geometrical changes which is possible especially if there are many light atoms like hydrogen atoms as in the models. The order of the energy and the thermodynamic properties are found to be reproducible using different functional methods and basis sets but HOMO, LUMO, J -coupling, hyperpolarizabilities, and isotropic and anisotropic shielding are found to depend more on the type of the functional used rather than on the type of the basis set. The only significant similarity observed among the methods applied in computing hyperpolarizabilities is that they all rated models Ru-S, Ru-Cl, and Ru-O among their best three. The optimized geometries and the thermodynamic properties obtained from the functional PBE are found to be very similar to MP2 and perform better than B3LYP and CCSD which further give insight into many literatures' preference for PBE in optimizing metal complexes. In computation of the isotropic and anisotropic shielding tensors, B3LYP gives

values similar to MP2 and performs better than PBE. The IR vibrations and assignment clearly show that the vibrations obtained from the MP2 and CCSD methods are very similar and give preference to the torsional and bending vibrations of the molecules over their stretching. The order of the IR vibrations of the ruthenium-ligand bonds can be assumed as Ru-N > Ru-O > Ru-C > Ru-Cl > Ru-S > Ru-P.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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