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Comparative DFT Study of a Ruthenium Complex

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Abstract: A comparative density functional theory (DFT) study of the Ruthenium complex (pentamethylcyclopentadienyl)(diisopropylmethylphosphine)(chloro)(trichlorosilyl)ruthenium hydride is reported. The molecule contains a ruthenium (Ru) atom, which, like other transition metals, is computationally difficult to handle due to the near degeneracy of their electronic states. Calculations were carried out in the gas phase using GAMESS software (the General Atomic and Molecular Electronic Structure System), which is an ab-initio quantum chemistry package. Five different basis sets were used, namely: Sapporo non-relativistic SPK DZP, SBKJ, 3-21G, STO3G, and STO6G. The molecule was optimized in quintuplicate with each of the basis sets. The computational results were compared with real X-ray data to assess how well the basis sets worked for a molecule containing a transition metal such as ruthenium. As the most computationally expensive basis set, the Sapporo non-relativistic SPK DZP was expected to give the most accurate results. However, unexpectedly, 3-21G, a computationally cheaper basis set, exhibited the best performance.

Keywords: SBKJ, 3-21G, STO-6G, Ruthenium, DFT.

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INTRODUCTION

Density functional theory (DFT), as the most common computational method for molecular calculations, has been used for decades to investigate the properties of molecules and molecular systems by ab-initio calculations. (1–6) It has been applied to a wide range of real atomic systems, including transition metal (TM) complexes. (3,7–11) However, it is well known that TM complexes are computationally difficult as they have unique properties, such as near degenerate electronic states, which lead to less accurate computational results than for other atomic types. (8–11) Nonetheless, DFT is still the most used computational approach as there is no better alternative (with a lower computational cost and better accuracy) available. (6)

Owing to the errors that arise in quantum chemical calculations of TM complexes, it is necessary to investigate suitable computational methods to minimize calculation errors. One of the most effective ways of determining the effectiveness of computational methods is to compare their results with real experimental data. By doing so, we aim to contribute to search for better parameter sets that give better results for ab-initio quantum chemical calculations of TM complexes, and also to contribute to the improvement of computational approaches by adding some new data to the existing literature.

Scientists need to know how much improvement they can expect from using a more computationally expensive model (for instance, when computation time is doubled). Therefore, expected improvements in accuracy with increased computational resources need to be investigated in order to decide if a particular model is worthwhile. The most effective way of doing this is to carry out comparative studies with new models and real data and contribute to the available literature, as with the current study. Moreover, these types of studies should include models that are both computationally cheap and expensive for comparison and accuracy. Hence, the

main aim of the current work is to determine the effectiveness of the computationally expensive Sapporo non-relativistic SPK DZP and SBKJ basis sets by comparison to the computationally cheaper STO3G, STO6G, and 3-21G.

The CAM-B3LYP functional, which was recently introduced, solves the long-range self-interaction error problem with its range-separated structure.(12,13) Furthermore, it has been used for transition metal complexes in previous studies.(14–17) Hence, it was also selected for investigation in our current study. As our results showed, it is an efficient functional for optimization of the ruthenium complex since it gave tolerable bond length errors according to the comparison of the calculated results with the real X-ray data, even for the computationally cheaper basis sets.

Here, five different basis sets were investigated for the optimization of the structure of (pentamethylcyclopentadienyl) (diisopropylmethylphosphine)(chloro) (trichlorosilyl)ruthenium hydride, and the calculated results were compared against real X-ray data for the molecule.(18)

MATERIALS AND METHODS

All calculations were carried out using GAMESS software (the General Atomic and Molecular Electronic Structure System), which is an ab-initio quantum chemistry package.(6,19) The hybrid Becke three-parameter Lee–Yang–Parr, modified by the Coulomb-attenuating method (CAM-B3LYP) was selected for this work as exchange correlation functional.(12) Five different basis sets were used to optimize the structure of the molecule: SBKJ (Stevens, Bash, Krauss, and Jasien) valence, Sapporo non-relativistic SPK DZP, 3-21G, STO3G, and STO6G.(20–24) All calculations were performed in the gas phase and all of the optimizations started from the same molecular configuration. All of the computational parameters were kept the same for all calculations, except for the basis sets. After the optimizations, frequency calculations were also carried out with the same levels of theory to confirm that were no imaginary frequencies, hence the optimized conformations are confirmed as real minima on the potential energy surface.

RESULTS AND DISCUSSION

The optimized geometry of the molecule is given in Figure 1. As can be seen in Figure 1, Ru is bonded to five ring carbons (C1, C2, C3, C6, C48) and four other atoms (Si27, P26, Cl32, and H31) in half-sandwich form.

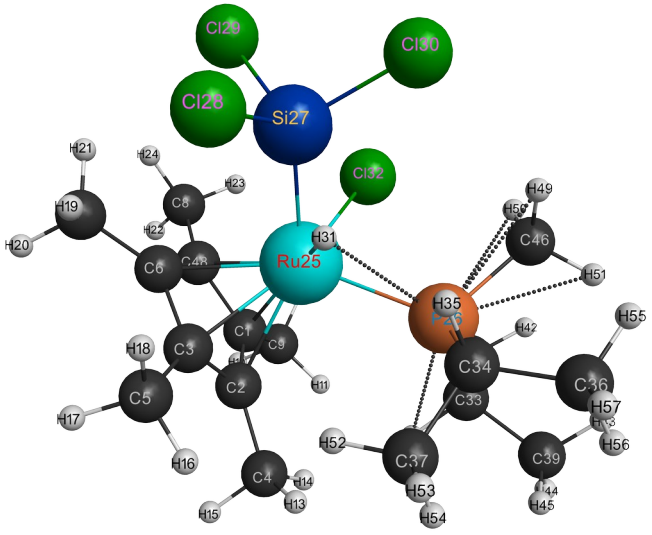

Figure 1: Optimized geometry of the molecule, as determined by the Sapporo non-relativistic SPK DZP basis set.

The calculated bond lengths of the molecule are given in Table 1, and the percentage of calculation errors for each bond and each method are presented in Table 2. As can be seen from Tables 1 and 2, the overall performance of the basis sets varies greatly, while the performance of individual basis sets also varies with the type of bonded atom. For instance, according to Table 1, the STO-6G basis set gives better performance than the STO-3G basis set for all of the bonds. Besides, STO-6G gives more errors for Ru bonds (with near 25%) than the C-C bonds (with near 4%).

Table 1: Bonded atoms and bond lengths calculated using basis sets and determined experimentally with X-ray data.

Atom 1	Atom 2	X-ray (Å)	SBKJ (Å)	Sapporo SPK DZP (Å)	3-21G (Å)	STO-3G (Å)	STO-6G (Å)
C1	C2	1.414	1.425	1.419	1.407	1.508	1.356
C1	C9	1.496	1.512	1.495	1.495	1.527	1.514
C2	C4	1.484	1.513	1.496	1.499	1.517	1.517
C3	C2	1.441	1.449	1.427	1.447	1.351	1.519
C3	C5	1.497	1.516	1.499	1.500	1.519	1.524
C3	C6	1.442	1.453	1.439	1.454	2.102	1.474
C33	C38	1.530	1.548	1.534	1.544	1.557	1.554
C33	C39	1.532	1.546	1.529	1.539	1.552	1.553
C34	C36	1.525	1.546	1.531	1.540	1.554	1.554
C34	C37	1.526	1.545	1.527	1.540	1.555	1.551
C48	C1	1.447	1.464	1.443	1.465	1.467	1.565
C48	C8	1.496	1.510	1.493	1.495	1.487	1.522
C6	C48	1.415	1.428	1.414	1.417	1.768	1.454
C6	C7	1.500	1.514	1.496	1.499	1.466	1.502
P26	C33	1.861	1.875	1.861	1.852	1.884	1.913
P26	C34	1.848	1.880	1.868	1.857	1.889	1.905
P26	C46	1.822	1.841	1.820	1.821	1.857	1.859
Ru25	C1	2.316	2.335	2.252	2.365	1.638	2.507
Ru25	C2	2.345	2.365	2.309	2.400	2.310	2.548
Ru25	C3	2.229	2.256	2.233	2.234	1.591	1.679
Ru25	C48	2.241	2.280	2.240	2.281	1.578	1.638
Ru25	C6	2.240	2.284	2.262	2.270	1.458	1.654
Ru25	Cl32	2.413	2.449	2.430	2.427	1.679	1.752
Ru25	P26	2.369	2.440	2.410	2.377	4.890	1.785
Ru25	Si27	2.315	2.374	2.341	2.307	1.767	1.833
Si27	Cl28	2.099	2.134	2.127	2.102	2.040	2.054
Si27	Cl29	2.089	2.105	2.093	2.066	2.044	2.043
Si27	Cl30	2.092	2.110	2.089	2.075	2.055	2.049

Table 2: Percentage calculation errors for each bond by basis set.

Atom 1	Atom 2	Error % SBKJ	Error % Sapporo SPK DZP	Error % 3-21G	Error % STO-3G	Error % STO-6G
C1	C2	0.78	0.35	-0.50	6.65	-4.10
C1	C9	1.07	-0.07	-0.07	2.07	1.20
C2	C4	1.95	0.81	1.01	2.22	2.22
C3	C2	0.56	-0.97	0.42	-6.25	5.41
C3	C5	1.27	0.13	0.20	1.47	1.80
C3	C6	0.76	-0.21	0.83	45.77	2.22
C33	C38	1.18	0.26	0.92	1.76	1.57
C33	C39	0.91	-0.20	0.46	1.31	1.37
C34	C36	1.38	0.39	0.98	1.90	1.90
C34	C37	1.25	0.07	0.92	1.90	1.64
C48	C1	1.17	-0.28	1.24	1.38	8.15
C48	C8	0.94	-0.20	-0.07	-0.60	1.74
C6	C48	0.92	-0.07	0.14	24.95	2.76
C6	C7	0.93	-0.27	-0.07	-2.27	0.13
P26	C33	0.75	0.00	-0.48	1.24	2.79
P26	C34	1.73	1.08	0.49	2.22	3.08
P26	C46	1.04	-0.11	-0.05	1.92	2.03
Ru25	C1	0.82	-2.76	2.12	-29.27	8.25

Ru25	C2	0.85	-1.54	2.35	-1.49	8.66
Ru25	C3	1.21	0.18	0.22	-28.62	-24.67
Ru25	C48	1.74	-0.06	1.78	-29.59	-26.91
Ru25	C6	1.96	0.98	1.34	-34.91	-26.16
Ru25	Cl32	1.51	0.73	0.60	-30.40	-27.38
Ru25	P26	2.98	1.72	0.32	106.39	-24.66
Ru25	Si27	2.54	1.12	-0.35	-23.68	-20.82
Si27	Cl28	1.67	1.33	0.14	-2.81	-2.14
Si27	Cl29	0.77	0.19	-1.10	-2.15	-2.20
Si27	Cl30	0.86	-0.14	-0.81	-1.77	-2.06

Figure 2 shows a comparison of the calculated C–C bond lengths with those obtained from the X-ray data, and Figure 3 shows the errors in the calculated C–C bond lengths. As shown in Figures 2 and 3, the Sapporo non-relativistic SPK DZP basis set gives the best approximation of the C–C bond lengths, while STO-3G gives the worst approximation. The most significant error for the C–C bond lengths was in relation to the C6 position calculated using the STO-3G basis set; 45% error was seen for the C3–C6 bond and 24% for the C6–C48 bond. On the other hand, when we look at the overall picture in Figure 2, it is clear that all of the approximations are in tolerable agreement with the C–C bond lengths determined via X-ray data, except for those obtained using the STO-3G basis set.

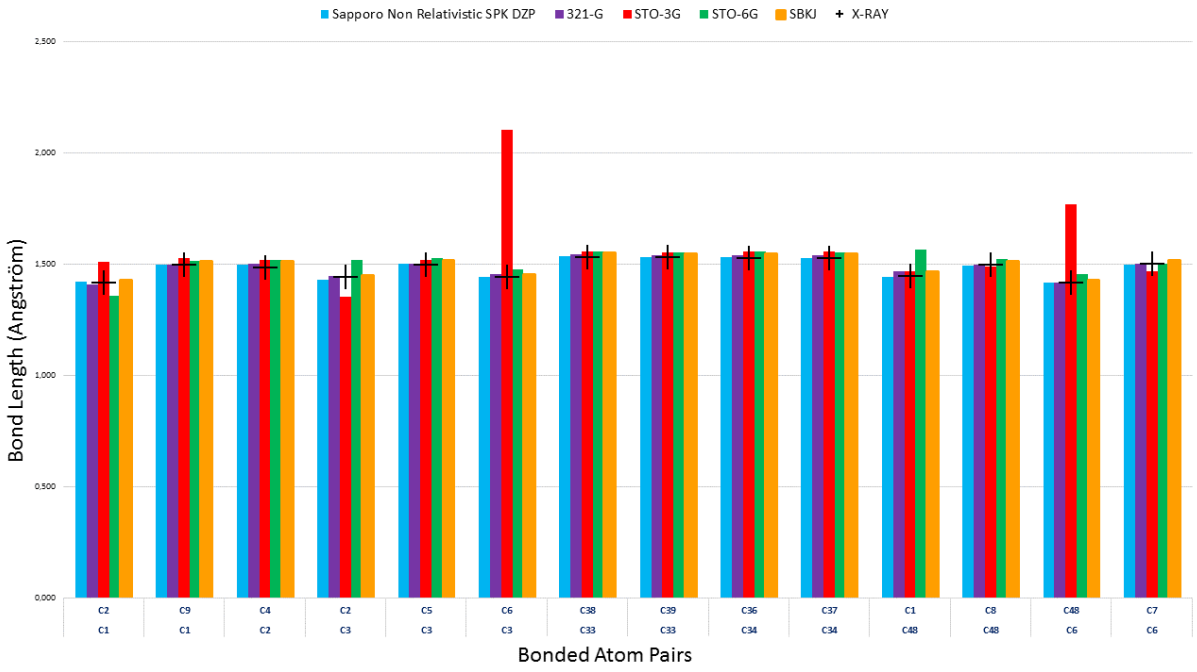

Figure 2: Comparison of calculated C–C bond lengths with those obtained from X-ray data.

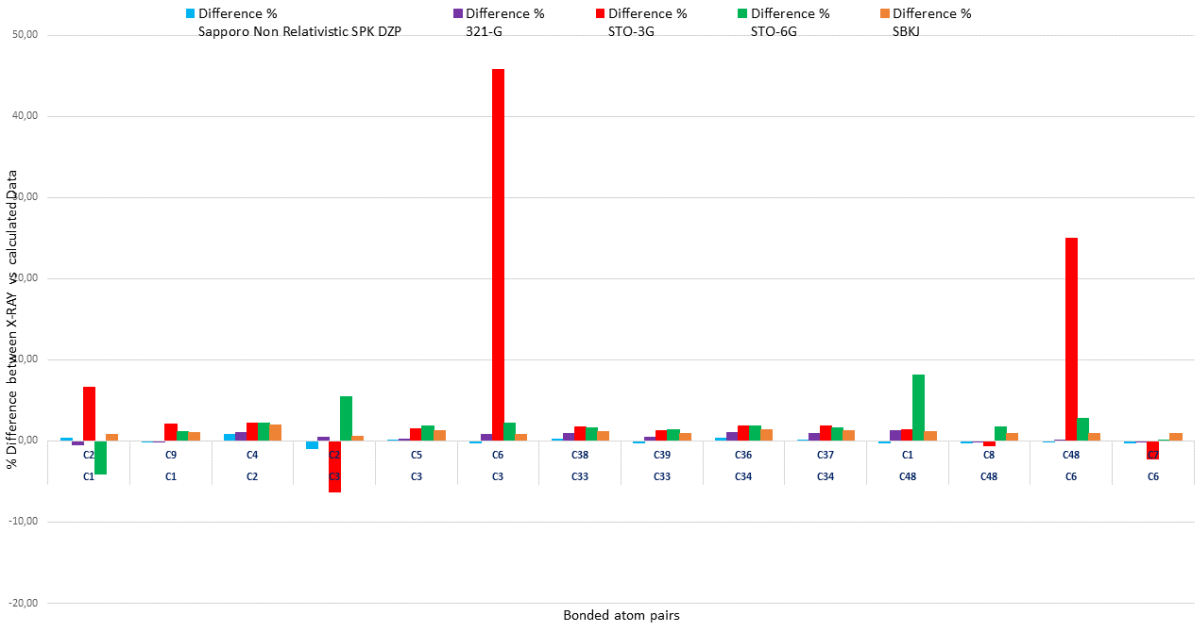

Figure 3: Percentage differences between calculate and experimentally determined C–C bond lengths.

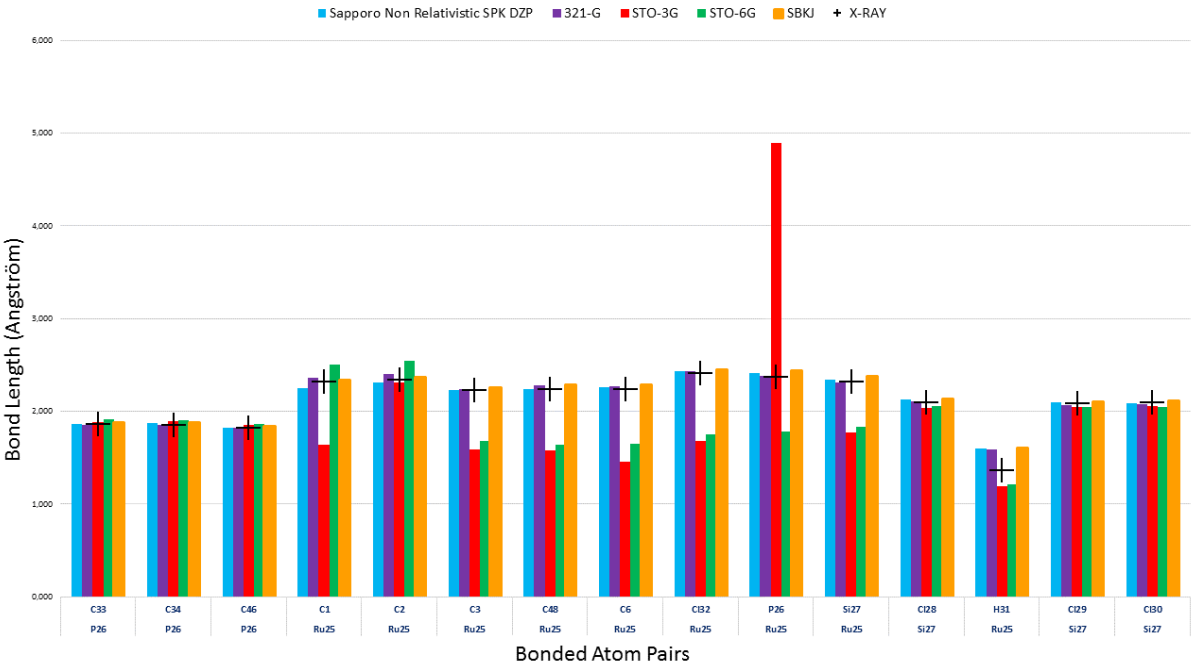

Figure 4: Comparison of calculated bond lengths for Ru, Si, Cl, and P atoms with those obtained from X-ray data.

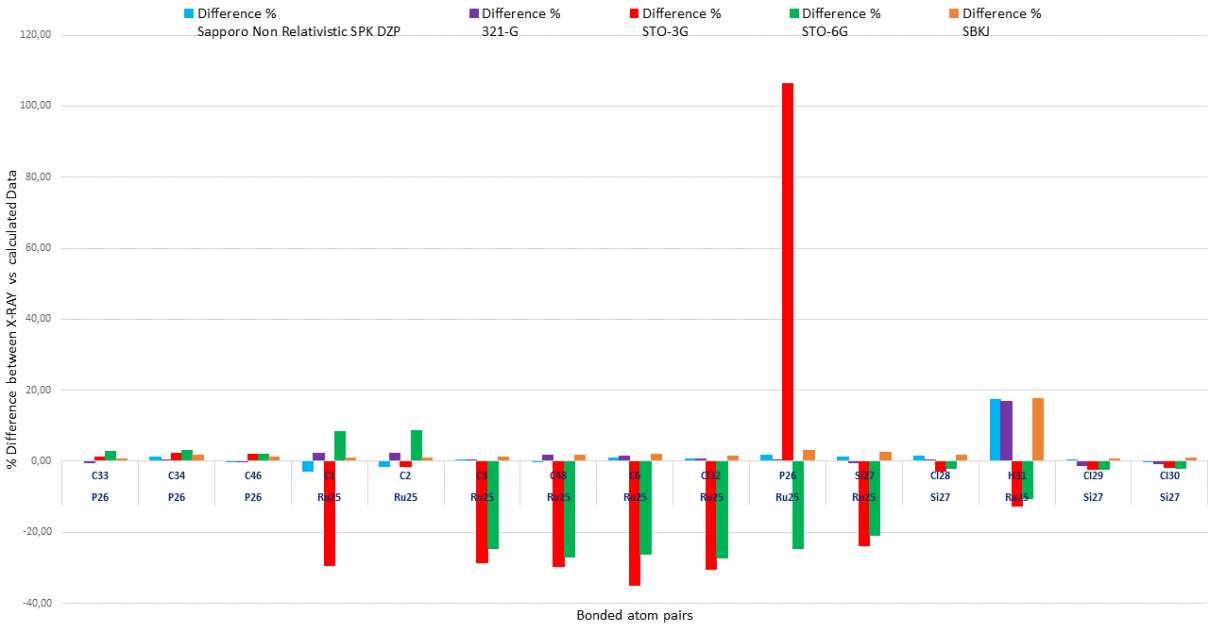

Figure 5: Percentage differences between calculate and experimentally determined bond lengths for Ru, Si, Cl, and P atoms.

Figure 4 shows a comparison of the calculated and experimentally obtained bond lengths for Ru, Si, Cl, and P atoms, while Figure 5 shows the percentage errors for these calculated bond lengths. It can be clearly seen that the performance of the basis sets differs significantly for Ru bonds, while closer agreement was observed for P–C and Si–Cl bonds. Clearly, neither of the Slater-type orbital basis sets (STO-3G nor STO-6G) give a good fit for Ru bonds. Although the STO-6G basis set shows better performance than the STO-3G, as expected, both approximations give intolerable errors for Ru bonds. Thus, this type of basis set is not recommended for quantum chemical calculations for complexes with transition metals such as Ru. The best performance for Ru bonds surprisingly came from 3-21G, a computationally cheaper method, rather than from the more computationally expensive Sapporo non-relativistic SPK DZP or SBKJ basis sets.

Figure 6 shows a comparison of the calculated and experimentally determined C–H bond lengths, and Figure 7 shows the percentage errors for the calculated C–H bond lengths. The results show that each of the five basis sets gave larger errors for H atoms than for any other atoms. All of the basis sets gave longer bond lengths than those obtained from the X-ray data for all H bonds.

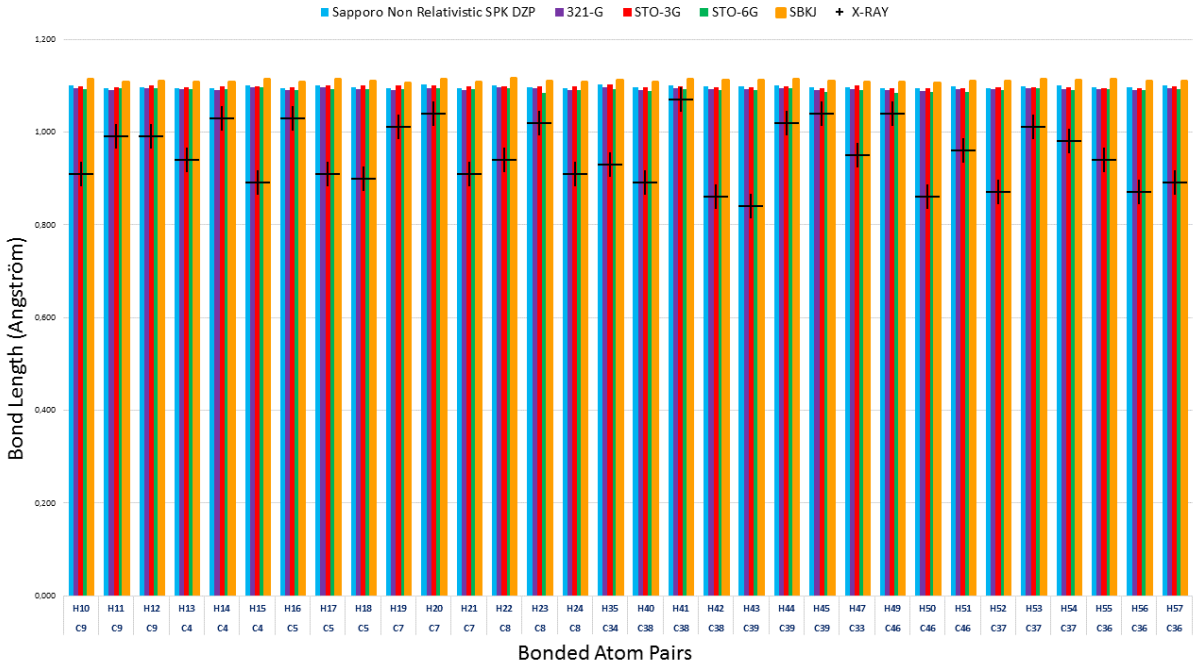

Figure 6: Comparison of calculated C–H bond lengths with those obtained from X-ray data.

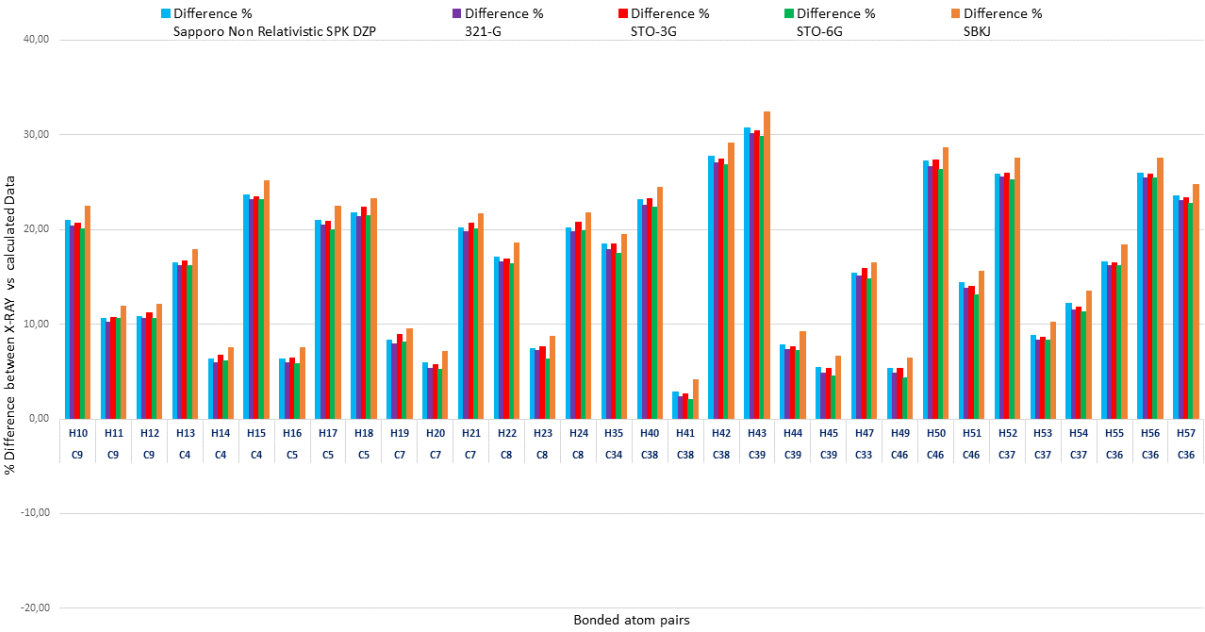

Figure 7: Percentage errors for calculated C–H bond lengths.

The calculation times and RMS (Root Mean Square) errors for specific bond types are presented in Table 3. The table shows that the fastest method is STO-3G with 604 minutes; hence, it is the cheapest method in a computational sense. However, STO-3G is the worst method when considering the percentage errors for all bond types.

On the other hand, the Sapporo non-relativistic SPK DZP basis set is the slowest one at 5290.2 minutes, requiring an eight-fold longer calculation time than STO-3G. The Sapporo non-relativistic SPK DZP basis is the most computationally expensive method used in this work. Although it gave the most accurate results for C–C bond lengths, as expected, this was unexpectedly not the case for Ru bonds or C–H bonds.

Surprisingly, 3-21G, the second-cheapest method in computational terms with 640.7 minutes, gave the

most accurate results for Ru bonds with a 4.501% RMS error, and the second-most accurate results for C–C and C–H bonds with results very close to those obtained using the best-performing basis set. Hence, when all of the bonds are considered with total RMS errors, 3-21G exhibits the best performance, being superior to the other more computationally expensive basis sets.

Table 3: The RMS error percentages for bonded atom groups and the calculation times.

Basis Set	Total calculation time (min)	Total RMS error	C–C bonds RMS error	Ru bonds RMS error	C–H bonds RMS error
Sapporo SPK DZP	5290.2	13.057	0.401	4.636	17.735
3-21G	640.7	12.722	0.687	4.501	17.275
STO-3G	604.0	22.059	14.221	33.428	17.623
STO-6G	1517.7	14.974	3.256	16.530	17.005
SBKJ	1300.9	13.983	1.124	4.795	18.968

The performance of each of the basis sets is shown graphically in Figure 8, which shows all the calculation times and the RMS error percentages for all bond types and all basis sets. Thus, we can compare both the calculation times and the errors simultaneously to compare the performances of all basis sets. Clearly, the Sapporo non-relativistic SPK DZP and the 3-21G basis sets have similar error rates for all types of bonds, while there is a large gap between their calculation times (88.17 hour vs. 10.68 hour).

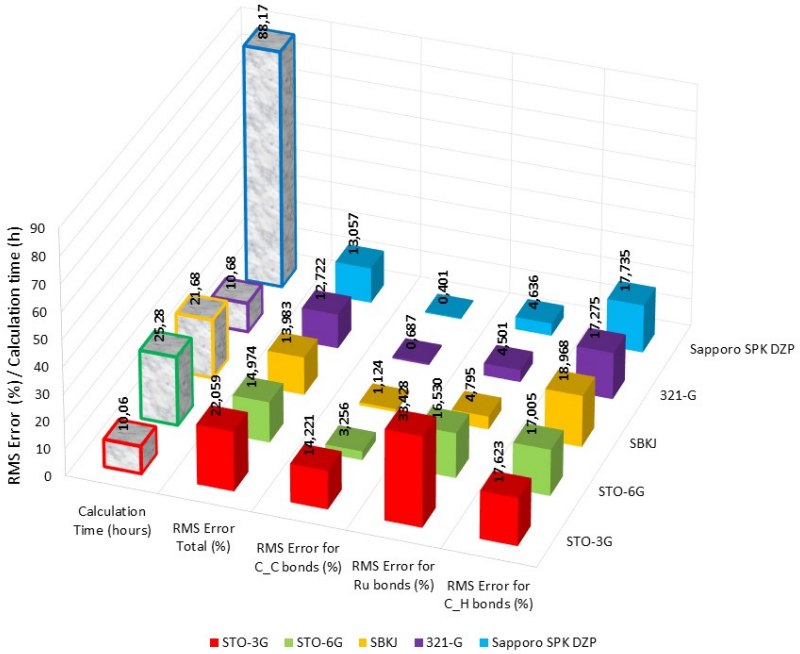

Figure 8: 3D graph comparing the performance of the basis sets, showing the RMS error percentages and calculation times for each basis set and each bond type.

CONCLUSIONS

Considering the overall picture in Figure 8, the following conclusions can be drawn:

a) Slater-type orbital (STO -*G) basis sets are not recommended for complexes involving Ru and similar transition metals.

b) All of the tested methods exhibited some difficulties in calculating H bonds, but the Slater-type orbital basis sets (STO-6G and even STO-3G) performed better than the other tested basis sets. STO-6G gives the smallest RMS error for H bonds, as seen in Figure 8.

c) The Sapporo non-relativistic SPK DZP, 3-21G, and SBKJ valence basis sets give similar error rates for C–C and Ru bonds, but with radically different calculation times of 5290.2 min, 640.7 min, and 1300.9 min, respectively.

d) Hence, among those tested in this work, the 3-21G basis set shows the best performance with a short computation time and high accuracy, and it is recommended for use for complexes with Ru and similar transition metals.

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