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Method and Basis Set Analysis of Oxorhenium(V) Complexes for Theoretical Calculations

Dustin Wayne Demoin, Yawen Li, Silvia S. Jurisson, and Carol A. Deakyne

Department of Chemistry, University of Missouri-Columbia, 601 S. College Avenue, Columbia, Missouri 65211-7600.

Abstract

A variety of method and basis set combinations has been evaluated for monooxorhenium(V) complexes with N, O, P, S, Cl, and Se donor atoms. The geometries and energies obtained are compared to both high-level computations and literature structures. These calculations show that the PBE0 method outperforms the B3LYP method with respect to both structure and energetics. The combination of 6-31G** basis set on the nonmetal atoms and LANL2TZ effective core potential on the rhenium center gives reliable equilibrium structures with minimal computational resources for both model and literature compounds. Single-point energy calculations at the PBE0/LANL2TZ,6-311+G* level of theory are recommended for energetics.

Keywords

Method calibration; autoscale values; complexation energy; rhenium; DFT; radiopharmaceutical

1. Introduction

Rhenium, the 5d transition metal congener of technetium, is a candidate for use in therapeutic radiopharmaceuticals. Chelates containing radioactive isotopes of rhenium have been used as radiopharmaceuticals for bone cancer pain palliation [1]. Because of the similar chemistry between rhenium and technetium and the lack of a non-radioactive isotope of technetium, imaging drug candidates that employ technetium have been characterized by using non-radioactive rhenium as a model for structural investigations [2-4]. In radiopharmaceutical preparations, radioactive rhenium(VII) is often supplied as the perrhenate ion (ReO_4^-). The rhenium atom in the perrhenate ion is coordinatively saturated by the oxygen atoms; thus, radiopharmaceutical preparations first reduce the rhenium to 5+, 3+, or 1+, where rhenium(V) is the most accessible of these oxidation states. Rhenium(V) radiopharmaceutical chemistry is dominated by oxo-chemistry, which utilizes the oxorhenium(V) core as the basis of ligand complexation. Monooxorhenium(V) complexes are generally square pyramidal when coordinated to four heteroatoms, but do sometimes have a solvent molecule or anion trans to the oxo-group to give a distorted octahedral geometry [5].

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Carol A. Deakyne, Department of Chemistry, University of Missouri, 125 Chemistry Building, 601 S. College Avenue, Columbia, MO 65211-7600; Telephone: (573)882-1347; Fax: (573)882-2754; DeakyneC@missouri.edu..

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Supplementary Information Available

Formation of a thermodynamically stable and kinetically inert metal complex to prevent the loss of the metal ion in vivo and reduce radiation damage to non-target tissues is of paramount importance for use of metal complexes as radiopharmaceuticals. Quantum chemical calculations of metal-ligand complexes allow for an in silico approach to identify which interactions help to stabilize the metal ion and which interactions might be improved. Moreover, the calculations may lead to a better understanding of why certain complexes are observed experimentally.

Previous calculations of rhenium-containing complexes have utilized the B3LYP functional and an assortment of basis sets [6-10]. Gancheff et al. focused on thiolato ligands bound to an oxorhenium(V) core and found that the PBE0 method and a mixed basis set [Stuttgart-Dresden (SDD) effective core pseudopotential (ECP) on the rhenium atom with a Midi! basis set on the nonmetal atoms] allowed for efficient computations yielding very good correlation to Re-S containing experimental structures [11]. Furthermore, Gancheff et al. discuss the utility of this method/mixed basis set combination for larger, more complex structures [11]. We are interested in examining new ligand systems with a variety of coordinating atoms (N, O, P, S, Cl, and Se) that may prove useful in radiopharmaceutical development. To our knowledge, an exhaustive computational study over a wide range of donor atoms to the oxorhenium(V) core has not been undertaken.

The structures and energetics of small model systems have been investigated to assess the reliability of combinations of mixed basis sets and the commonly employed B3LYP, PBE0, MP2, and CCSD(T) methods. The effectiveness of the mixed basis sets was further assessed by comparing calculated geometries to literature crystal structures.

2. Methods

2.1 Computational Details

As a first step in assessing the ability of the selected method/basis set combinations to provide reliable structures and energetics, ReOX_3 and ReOX_4^{1-} ($\text{X}^{1-} = \text{NH}_2^{1-}$; OH^{1-} ; PH_2^{1-} ; SH^{1-} ; Cl^{1-} ; and SeH^{1-}) model complexes were investigated. These complexes are denoted **M1-M12** (Fig. 1). As a second step, literature structures available in the Cambridge Crystallographic Data Centre (CCDC) [12] were investigated. Five complexes containing various heteroatoms bound to the oxorhenium(V) core were chosen on the basis of their simplicity/symmetry and/or their relevance to radiopharmaceuticals [13-16]. These five compounds are denoted **L1-L5** (Fig. 2). **L1** and **L2** are ReOS_4 systems, **L3** is a ReOSNOPCl system, **L4** is a $\text{ReOS}_2\text{N}_2\text{Cl}$ system, and **L5** is a ReOS_3C system. For all 17 complexes (**M1-M12** and **L1-L5**), full geometry optimizations and normal-mode vibrational frequency calculations were carried out at each calculational level considered. All of the calculations were performed using the *Gaussian03* or *Gaussian09* suite of programs [17, 18].

Included in this work are 1) series of basis sets derived from the 6-31G and 6-311G basis sets and 2) the recently developed basis sets that extend the LANL2DZ basis set for rhenium [9]. The latter basis sets have been investigated to a limited extent in the literature [19]. In addition, the aug-cc-pVTZ and aug-cc-pVTZ-pp (for Re) basis sets were assessed for model systems **M1-M12**. A complete list of the method and basis set combinations is found in Tables 1 and 2, along with the abbreviations that are used throughout this paper. These abbreviations are similar to those used by Gancheff et al.[11]

All symmetry permutations were considered at the B3LYP/LDZ level. That is, for the ReOX_3 model systems, structures with C_{3v} , C_3 , C_s , and C_1 symmetries were investigated. For the ReOX_4^{1-} model systems, structures with C_{4v} , C_4 , C_{2v} , C_2 , C_s , and C_1 symmetries were investigated. Additionally, for ReOCl_4^{1-} , structures with C_{3v} and C_3 symmetry

(trigonal bipyramidal) were investigated. Fig. 1 displays the global minima for **M1-M12** at the MP2/ACPTZ level and their respective symmetries. The other method and basis set combinations were employed only for the B3LYP/LDZ optimized conformations that had all real frequencies. For calculations of literature compounds, the initial geometries were generated from the cif file from the CCDC [12], but all possible isomeric forms were examined to ensure the global minimum was located.

Monooxorhenium(V) complexes are accepted to be singlet electronic states because of the ligand field splitting in the square pyramidal geometry [20]. Nevertheless, both singlet and triplet electronic states were analyzed to ensure that the singlet state is the lowest in energy. We found that only the ReOCl_3 complex is a ground-state triplet, so the quintet state (only at the B3LYP/LDZ level) was examined for this complex. Because the lowest energy quintet equilibrium structure is approximately 58 kcal/mol higher in energy than the lowest energy triplet, calculations with spin states higher than the quintet were not performed.

Two sets of single-point energy calculations were performed for model systems **M1-M12**. In the first set, PBE0/LDZ6311*, PBE0/LTZ6311*, PBE0/LTZf6311* with and without diffuse functions and/or selenium pseudopotentials, and SDD6311+* were obtained using the PBE0/LTZ6311** equilibrium structures. Additionally, the PBE0/LTZ6311**Se//PBE0/LTZ6311** results for the selenium model system were included in this set. In the second set, CCSD(T)/ACPTZ//MP2/ACPTZ energies were evaluated. The T1 diagnostic values, all less than 0.028 (Table 3), are sufficiently small to indicate single-reference character of the wavefunctions [21-23].

2.2 Goodness of Fit (GoF) Calculations

The equilibrium structures of the model systems were benchmarked against the structures derived from the highest level of theory and largest basis set employed for optimizations, MP2/ACPTZ. This choice is supported by numerous previous studies that have employed MP2 optimized or reoptimized structures as a reference for transition metal complexes, especially for (but not limited to) closed-shell, singlet species [24-33]. The computed structures of the literature compounds were compared directly to the experimentally determined crystal structures from the cif file from the CCDC [12]. For the goodness of fit (GoF) calculations of ReOCl_3 and ReOCl_4^{1-} , with no hydrogen atoms, to be consistent with those of the remaining systems, the 6-31G* results were summed twice and the 6-31+G* results were summed thrice for each method and rhenium effective core pseudopotential (ECP).

Purely structural GoF calculations were performed using the root-mean-square deviation (RMSD) calculator of the Visual Molecular Dynamics (VMD) 1.8.7 software package [34]. This program allows for the molecule to be rotated/aligned before calculating the RMSD of the location of each of the atoms from the designated reference [19, 35].

For intrasystem analysis of the GoF (to find an overall best method/basis set combination for a single model system or literature structure; e.g., $\text{ReO}(\text{OH})_3$), an autoscale approach was employed. Within the system of analogous structures, the RMSD values were averaged ($\text{VMD}_{\text{GoF}_{\text{avg}}}$) and the standard deviation (σ_{GoF}) was evaluated. Outliers were removed from the average and standard deviation calculations in this step if the RMSD value was double the average, when included in the average calculation, and above two standard deviations, when included in the standard deviation calculation. The autoscale value was calculated using:

$$\text{Autoscale}_{\text{VMD}} = \frac{\text{VMD}_{\text{GoF}_{\text{Method/BasisSet}}} - \text{VMD}_{\text{GoF}_{\text{avg}}}}{\sigma_{\text{GoF}}}. \quad (1)$$

An average autoscale intersystem value (AAIV) was calculated by averaging each of the groups (ReOX₃: **M1-M6**; ReOX₄¹⁻: **M7-M12**; and **L1-L5**) separately:

$$\text{Average Autoscale}_{\text{VMD}_{\text{intersystem}}} = \frac{\sum_i^n \text{Autoscale}_{\text{VMD}_i}}{n}. \quad (2)$$

2.3 Energy Calculations

For the model system complexation reactions,

the GoF data for the ReOX₄¹⁻ complexation energies were obtained as the absolute value of the difference between the CCSD(T)/ACPTZ//MP2/ACPTZ energy and that from the method/basis set employed (UE_{complexation}). These unsigned differences were averaged to calculate the mean unsigned error (MUE_{complexation}) and standard deviation (σ_{complexation}). The autoscale value was calculated using equation 4.

$$\text{Autoscale}_{\text{complexation}} = \frac{\text{UE}_{\text{complexation}_{\text{Method/BasisSet}}} - \text{MUE}_{\text{complexation}}}{\sigma_{\text{complexation}}} \quad (4)$$

Once these autoscale values were obtained, an average autoscale intersystem value was calculated by averaging each of the systems separately (ZPE-corrected ΔE, ΔH°, and ΔG°):

$$\text{Average Autoscale}_{\text{complexation}_{\text{intersystem}}} = \frac{\sum_i^n \text{Autoscale}_{\text{complexation}_i}}{n}. \quad (5)$$

3. Results and Discussion

Unlike previous studies that focused on one very similar/specific ligand field environment around the metal center [11, 36], a variety of ligands from three different groups on the periodic table (pnictogenides, chalcogenides, and halides) was evaluated. In so doing, a way to determine which method/basis set combination was the best fit for the variety of systems that would be encountered in our theoretical radiopharmaceutical calculations involving rhenium(V) as the dose delivering radionuclide was needed. The RMSD values of different systems were not generally similar enough in magnitude to merely take an average of these values to obtain an intersystem value for each method/basis set combination. Autoscaling, a process used routinely in analytical chemistry, was chosen to provide a more equitable approach for finding the best overall method and basis set for oxorhenium(V) ligand systems. The autoscaling parameter represents how many standard deviations the method/basis set combination is better or worse than the average of all of the combinations used. The smaller this value is (most negative), the better the calculation is than the average, whereas the larger the number (most positive), the worse the calculation is. An average of the autoscaled values then results in a balanced determination of the overall appropriate method and basis set. Note that having similar autoscale values does not imply that two structures are similar; it merely implies that the structures differ from the standard by which they are being assessed by the same amount.

3.1 Structure of Model Systems: ReOX_3 and ReOX_4^{1-}

The equilibrium geometry for each ReOX_3 and ReOX_4^{1-} model system at the MP2/ACPTZ level is depicted in Fig. 1. The MP2/ACPTZ geometric parameters for each model system are given in the supplementary information, along with the corresponding Cartesian coordinates obtained (Section S6). Although the lowest energy conformations were reproduced by all method/basis set combinations, no one combination was closest to the optimized MP2/ACPTZ structure in all cases.

Table 4 lists the top 20 structural average autoscaled intersystem values (AAIV) for the DFT method and basis set combinations. For convenience, a numerical rank is given for the entries in Table 4 and in all other tables for which ranking is relevant. A complete list of the AAIV for all of the methods and basis sets used (except for the special selenium basis sets) is found in the supplementary information (Table S4). With 19 out of the top 20 ranked AAIV, the PBE0 method overall outperforms the B3LYP method in describing optimized rhenium geometries (Table 4), which is consistent with the findings of Gancheff et al. for thiolato ligands [11]. The SDDMIDI basis set recommended by Gancheff et al. performed well for the $\text{ReO}(\text{SH})_4^{1-}$ model system [11], but not better than other basis sets employed with PBE0 (Table S4). PBE0 computations take approximately the same amount of time as B3LYP calculations, so the use of the PBE0 method should not adversely affect computational efficiency. Additionally, Zhao and Truhlar have shown that PBE0 outperforms B3LYP for nonbonding interactions [37], which might be of greater importance in future studies of systems with peptide hydrogen-bonding frameworks and metal interactions.

Out of the basis sets combined with the PBE0 method, the most complete basis set—ACPTZ—corresponds most closely to the MP2/ACPTZ results (Table 4). Even for the model systems, however, the PBE0/ACPTZ computation required significantly more processor time than did the other PBE0 computations, which would only compound in larger, asymmetric systems. As such, the much faster calculation with the LTZ631** basis set combines a good structure optimization for both the ReOX_3 and ReOX_4^{1-} species with minimal processor time usage. The PBE0/LTZ631** geometry optimizations utilize a triple- ζ valence basis set with an ECP for the rhenium center and the generally accepted 6-31G** double- ζ basis set for the nonmetal atoms.

Spurious or inconsistent results and alignment problems were encountered for some of the model systems, namely $\text{ReO}(\text{NH}_2)_3$, $\text{ReO}(\text{OH})_3$, $\text{ReO}(\text{OH})_4^{1-}$, $\text{ReO}(\text{SeH})_3$ and $\text{ReO}(\text{SeH})_4^{1-}$. The problematic points raised by these systems are as follows (data not shown for $\text{ReO}(\text{NH}_2)_3$, $\text{ReO}(\text{OH})_3$ and $\text{ReO}(\text{OH})_4^{1-}$).

$\text{ReO}(\text{NH}_2)_3$ Structure—The VMD program seemed to have difficulties aligning the $\text{ReO}(\text{NH}_2)_3$ B3LYP and PBE0 structures to the MP2/ACPTZ structure. The RMSD values for the $\text{ReO}(\text{NH}_2)_3$ system were orders of magnitude greater than those of the other ReOX_3 systems (the reason autoscaled values were used to obtain intersystem values). The RMSD values were also much greater than warranted by the structural deviations. For these reasons, the DFT RMSD values and MP2 RMSD values were not directly comparable.

$\text{ReO}(\text{OH})_3$ Structure—With this system, the LDZ, SDD, and SDDMIDI results were at least five standard deviations above the average. Thus, these six data points (three basis sets for both B3LYP and PBE0) were removed when calculating the average and standard deviation.

$\text{ReO}(\text{OH})_4^{1-}$ Structure—When directly comparing B3LYP and PBE0 results, the calculations without diffuse functions performed better with the B3LYP method, whereas

PBE0 performed better when diffuse functions were included. This change may be an artifact of the hydroxide model system because the diffuse functions might allow for a better description of the hydrogen-bonding interactions that occur in this system, which PBE0 better models than B3LYP.²⁴

ReO(SeH)₃ and ReO(SeH)₄¹⁻ Structures—Table 5 lists the top 10 DFT RMSD results for the ReO(SeH)₃ and ReO(SeH)₄¹⁻ systems and gives their individual rankings relative to the MP2/ACPTZ structure. Spurious results obtained when calculating the complexation energies for these model systems required the use of additional basis sets (Table 2). None of these additional basis sets significantly outperformed the basis sets originally used for the geometry optimizations for the selenium model systems. Again, the ReO(SeH)₄¹⁻ geometry is well defined by the medium-sized LTZ631** basis set, and this basis set does a respectable optimization for the ReO(SeH)₃ geometry as well. Therefore, the LTZ631** basis set is adequate for geometry optimizations, but single-point energy calculations are required for energetic data, as discussed below.

3.2 Complexation Energy Calculations of Model Systems: ReOX₃ and ReOX₄¹⁻

The closest 20 DFT method and basis set combinations with respect to the average autoscale intersystem values for the complexation reactions (AAIVCR, equation 5) are collected in Table 6. Supplementary material Table S6a-c presents the results for all of the method and basis set combinations investigated. The best method and basis set combination for the geometry optimization calculations, PBE0/LTZ631**, did not perform well for the complexation energy calculations (Table S6a-c). The calculations including diffuse functions on the non-hydrogen atoms improves the agreement with the complexation energy values obtained using CCSD(T)/ACPTZ//MP2/ACPTZ.

The double- ζ basis sets for the selenium model system yielded positive complexation energies (e.g., using the PBE0/LTZ631** basis set gives a $\Delta E_{\text{complex}}$ value of 223.3 kcal/mol). Interestingly, however, the selenium $\Delta E_{\text{complex}} = -76.9$ kcal/mol when calculated at the PBE0/LDZ level. Inclusion of an ECP on the selenium centers yielded negative complexation energies. Table 7 indicates the top 10 DFT/basis set combinations for calculating the SeH¹⁻ model system complexation energies, which now includes the PBE0/LTZ631**Se value ranked fourth with respect to the CCSD(T)/ACPTZ//MP2/ACPTZ value.

In order to identify an efficient and reliable method/basis set combination with respect to complexation energies for the complete set of coordinating atoms, a series of single-point energies was calculated using the PBE0/LTZ631** equilibrium geometries. Table 8 gives the mean unsigned errors obtained with these single-point energy calculations with respect to the CCSD(T)/ACPTZ//MP2/ACPTZ results. The complete set of single-point energy results is provided in Table S8. The lowest values of $\Delta \Delta E_{\text{MUE}}$, $\Delta \Delta H^{\circ}_{\text{MUE}}$, and $\Delta \Delta G^{\circ}_{\text{MUE}}$ were obtained with either the PBE0/LDZ6311+*Se//PBE0/LTZ631** or PBE0/LTZ6311+*Se//PBE0/LTZ631** levels of theory, which are not significantly different from the PBE0/LTZ6311+*Se//PBE0/LTZ631** results. The magnitudes of the MUEs depends strongly on inclusion of diffuse functions in the basis set, but are essentially independent of the choice of rhenium pseudopotential. The diffuse functions are most important for reproducing the CCSD(T)/ACPTZ NH₂¹⁻ and OH¹⁻ binding affinities as well as the overall trend in binding affinities, especially with respect to the PH₂¹⁻ and NH₂¹⁻ complexes (Table S8). Although important at the lower levels of theory, the inclusion of pseudopotentials on the selenium centers does not significantly influence the overall MUEs at these levels of theory (Table 8). On the basis of these results, the recommended level for calculating complexation energies is PBE0/LTZ6311+*Se//PBE0/LTZ631**.

The hydroxide interaction is calculated to be the strongest of the model systems (Table S8), perhaps due to the high electronegativity of oxygen pulling electron density away from the metal center. If this is the case, then the fourth Re-OH bond will have more ionic character and should be a stronger interaction. However, decreasing electronegativity does not directly coincide with weaker bonds to the metal center, as evidenced by PH_2^{1-} calculated as being more strongly bound than Cl^{1-} , NH_2^{1-} , SH^{1-} , and SeH^{1-} .

3.3 Literature Crystal Structure Results

The equilibrium geometry for each literature structure (**L1-L5**) at the PBE0/LTZ631** level is depicted in Fig. 2. The PBE0/LTZ631** geometric parameters for each literature structure are given in the supplementary information, along with the corresponding Cartesian coordinates (Section S7). Table 9 shows the relative autoscale RMSD values (equation 2) for the subset of method and basis set combinations employed for the five literature structures [13-16] from Fig. 2. Overall, the average autoscaled intersystem values indicate that the gas phase PBE0/LTZ631** equilibrium geometry is in good agreement with these solid-state crystal structures suggesting that crystal packing effects and the presence of counter ions (if applicable) are not significantly affecting the structures. More generally, the PBE0 method again outperforms the B3LYP method.

Compound **L4** was optimized with the nitrogen atoms of the coordinating ligands in both cis and trans equatorial positions with the PBE0 method and the rhenium LDZ ECP basis sets (LDZ631*, LDZ631**, LDZ631+*, LDZ631+**, and LDZ631+**) [38]. Each of these method/basis set combinations found the cis arrangement (Fig. 2), which coincides with that of the crystal structure, to be the lowest energy configuration by approximately 11 kcal/mol. The results support screening at a lower level of theory to determine the thermodynamically more stable species.

4. Conclusions

Overall, the PBE0 method outperforms the B3LYP method in reproducing the MP2/ACPTZ geometries and complexation energies for the rhenium complexes computed herein, which mirrors previous results [11, 39, 40]. Our results indicate that the best overall method and basis set, in terms of efficiency and reliability, for computing the geometry of the monooxorhenium(V) complexes is PBE0/LTZ631**. Geometry optimizations of selenium complexes are best performed with an all-electron basis set rather than using an ECP for the selenium atom. For the selenium-containing complexes, a single-point energy calculation on the PBE0/LTZ631** equilibrium structure is imperative to obtain a meaningful value for the complexation energy. Overall, the recommended method/basis set combination for single-point energy calculations is PBE0/LTZ631+*Se//PBE0/LTZ631**.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References and Notes

- Ogawa K, Mukai T, Arano Y, Otaka A, Ueda M, Uehara T, Magata Y, Hashimoto K, Saji H. Rhenium-186-monoaminemonoamidedithiol-conjugated bisphosphonate derivatives for bone pain palliation. *Nucl. Med. Biol.* 2006; 33:513–520. [PubMed: 16720243]
- Mahmood, A.; Kuchma, MH.; Freiberg, E.; Goldstone, J.; Davison, A.; Jones, AG. Functionalized Tetradentate N_2S_2 Chelates and their Technetium-99 and Rhenium Complexes: Synthesis, Spectroscopy, and Structural Characterization. In: Nicolini, M.; Mazzi, U., editors. *Technetium, Rhenium and Other Metals in Chemistry and Nuclear Medicine*. Academia Cusanus; Bressanone, Italy: 1999. p. 253-257.
- Ono M, Ikeoka R, Watanabe H, Kimura H, Fuchigami T, Haratake M, Saji H, Nakayama M. Synthesis and Evaluation of Novel Chalcone Derivatives with $^{99m}Tc/Re$ Complexes as Potential Probes for Detection of -Amyloid Plaques. *ACS Chem. Neurosci.* 2010; 1:598–607. [PubMed: 22778849]
- Davison A, Meltzer PC, Blundell P, Jones AG, Mahmood A, Garada B, Zimmerman RE, Holman BL, Madras BK. Technetium-99m SPECT imaging agent which targets the dopamine transporter in primate brain. *J. Med. Chem.* 1997; 40:1835–1844. [PubMed: 9191960]
- Greenwood, NN.; Earnshaw, A. *Chemistry of the Elements*. 2nd ed.. Elsevier Ltd.; Amsterdam: 1997.
- Machura B, Wolff M, Switlicka A, Gryca I. p-Tolylimido rhenium(V) complexes - Synthesis, X-ray studies, spectroscopic characterization and DFT calculations. *Polyhedron*. 2010; 29:2381–2392.
- Cheng MJ, Nielsen RJ, Ahlquist M, Goddard WA. Carbon-oxygen bond forming mechanisms in rhenium oxo-alkyl complexes. *Organometallics*. 2010; 29:2026–2033.
- Tia R, Adei E. Density functional theory studies of the mechanistic aspects of olefin metathesis reactions. *Dalton Trans.* 2010; 39:7575–7587. [PubMed: 20623044]
- Roy LE, Hay PJ, Martin RL. Revised Basis Sets for the LANL Effective Core Potentials. *J. Chem. Theory and Comput.* 2008; 4:1029–1031.
- Machura B, Kruszynski R, Jaworska M, Lodowski P. Crystal, molecular and electronic structure of the $[ReCl_3(bipy)(PPh_3)]$ complex. *Polyhedron*. 2005; 24:701–709.
- Gancheff JS, Denis PA, Hahn FE. Assessment of density functional methods for the study of vanadium and rhenium complexes with thiolato ligands. *J. Mol. Struct.: THEOCHEM*. 2010; 941:1–9.
- Cambridge Structural Database, in, The Cambridge Crystallographic Data Centre, 2004-2011.
- Clegg W, Boyde S, Garner CD. Structures of Tetraphenylphosphonium Bis(ethane-1,2-dithiolato)oxorhenium(V) and Tetraphenylphosphonium Bis(benzene-1,2-dithiolato)oxorhenium(V). *Acta Crystallogr.* 1988; C44:172–174.
- Mévellec F, Roucoux A, Noiret N, Patin H. Synthesis, properties and spectroscopic studies of rhenium(V) complexes stabilized by tridentate Schiff bases derived from S-methyl dithiocarbamate. *Dalton Trans.* 2001:3603–3610.
- Konno T, Shimazaki Y, Kawai M, Hirotsu M. Synthesis, Characterization, and Stereochemistry of Oxorhenium(V) Complexes with 2-Aminoethanethiolate. *Inorg. Chem.* 2001; 40:4250–4256. [PubMed: 11487329]
- Shan X, Ellern A, Guzei IA, Espenson JH. Syntheses and Oxidation of Methyloxorhenium(V) Complexes with Tridentate Ligands. *Inorg. Chem.* 2003; 42:2362–2367. [PubMed: 12665371]
- Frisch, MJ.; Trucks, GW.; Schlegel, HB.; Scuseria, GE.; Robb, MA.; Cheeseman, JR.; Montgomery, JJA.; Vreven, T.; Kudin, KN.; Burant, JC.; Millam, JM.; Iyengar, SS.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, GA.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, JE.; Hratchian, HP.; Cross, JB.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, RE.; Yazyev, O.; Austin, AJ.; Cammi, R.; Pomelli, C.; Ochterski, JW.; Ayala, PY.; Morokuma, K.; Voth, GA.; Salvador, P.; Dannenberg, JJ.; Zakrzewski, VG.; Dapprich, S.; Daniels, AD.; Strain, MC.; Farkas, O.; Malick, DK.; Rabuck, AD.; Raghavachari, K.; Foresman, JB.; Ortiz, JV.; Cui, Q.; Baboul, AG.; Clifford, S.; Cioslowski, J.; Stefanov, BB.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, RL.; Fox, DJ.; Keith,

- T.; Al-Laham, MA.; Peng, CY.; Nanayakkara, A.; Challacombe, M.; Gill, PMW.; Johnson, B.; Chen, W.; Wong, MW.; Gonzalez, C.; Pople, JA. Gaussian 03. Gaussian, Inc.; Wallingford, CT: 2004.
18. Frisch, MJ.; Trucks, GW.; Schlegel, HB.; Scuseria, GE.; Robb, MA.; Cheeseman, JR.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, GA.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, HP.; Izmaylov, AF.; Bloino, J.; Zheng, G.; Sonnenberg, JL.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, JJA.; Peralta, JE.; Ogliaro, F.; Bearpark, M.; Heyd, JJ.; Brothers, E.; Kudin, KN.; Staroverov, VN.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, JC.; Iyengar, SS.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, JM.; Klene, M.; Knox, JE.; Cross, JB.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, RE.; Yazyev, O.; Austin, AJ.; Cammi, R.; Pomelli, C.; Ochterski, JW.; Martin, RL.; Morokuma, K.; Zakrzewski, VG.; Voth, GA.; Salvador, P.; Dannenberg, JJ.; Dapprich, S.; Daniels, AD.; Farkas, O.; Foresman, JB.; Ortiz, JV.; Cioslowski, J.; Fox, DJ. Gaussian 09. Gaussian, Inc.; Wallingford CT: 2010.
 19. For rhenium the LANL2TZ and LANL08 ECPs are identical, as are the LANL2TZ(f) and LANL08(f) ECPs.
 20. Sigouin O, Beauchamp AL. Oxo-rhenium(V) complexes with 8-hydroxyquinoline derivatives. *Can. J. Chem.* 2005; 83:460–470.
 21. Jiang W, Deyonker NJ, Wilson AK. Multireference character for 3d transition-metal-containing molecules. *Journal of Chemical Theory and Computation*. 2012; 8:460–468.
 22. Riedel S, Renz M, Kaupp M. High-valent technetium fluorides. Does TcF₇ exist? *Inorganic Chemistry*. 2007; 46:5734–5738. [PubMed: 17569532]
 23. Lee TJ, Taylor PR. A diagnostic for determining the quality of single-reference electron correlation methods. *Int. J. Quantum Chem., Quantum Chem. Symp.* 1989; 23:199–207.
 24. Premkumar JR, Vijay D, Sastry GN. The significance of the alkene size and the nature of the metal ion in metal-alkene complexes: a theoretical study. *Dalton Transactions*. 2012; 41:4965–4975. [PubMed: 22407407]
 25. Youn IS, Kim DY, Singh NJ, Park SW, Youn J, Kim KS. Intercalation of Transition Metals into Stacked Benzene Rings: A Model Study of the Intercalation of Transition Metals into Bilayered Graphene. *Journal of Chemical Theory and Computation*. 2011; 8:99–105.
 26. Sadjadi S, Matta CF, Lemke KH, Hamilton IP. Relativistic-Consistent Electron Densities of the Coinage Metal Clusters M₂, M₄, M₄₂⁺, and M₄Na₂ (M = Cu, Ag, Au): A QTAIM Study. *The Journal of Physical Chemistry A*. 2011; 115:13024–13035. [PubMed: 21842915]
 27. Tsukamoto S, Sakaki S. Theoretical Study of Pt(PR₃)₂(AlCl₃) (R = H, Me, Ph, or Cy) Including an Unsupported Bond between Transition Metal and Non-transition Metal Elements: Geometry, Bond Strength, and Prediction. *The Journal of Physical Chemistry A*. 2011; 115:8520–8527. [PubMed: 21710982]
 28. Wijeratne AB, Gracia J, Yang SH, Kroll P, Armstrong DW, Schug KA. New structural insight for antimony(III)-tartrate. *Inorganic Chemistry Communications*. 2010; 13:1504–1508.
 29. Jeanvoine Y, Spezia R. Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺-Binding Chalcogen–Chalcogen Bridges: A Compared MP2 and B3LYP Study. *The Journal of Physical Chemistry A*. 2009; 113:7878–7887. [PubMed: 19522520]
 30. Donald KJ, Hargittai M, Hoffmann R. Group 12 Dihalides: Structural Predilections from Gases to Solids. *Chemistry – A European Journal*. 2009; 15:158–177.
 31. Mou CH, Witek HA. Theoretical study of noble-gas containing metal halides. *Journal of Chemical Physics*. 2008; 129
 32. Zhang P-X, Zhao Y-F, Hao F-Y, Zhang G-H, Song X-D, Li X-Y. Bonding analysis for NgMOH (Ng=Ar, Kr and Xe; M=Cu and Ag). *Molecular Physics*. 2008; 106:1007–1014.
 33. Olson RM, Varganov S, Gordon MS, Metiu H, Chretien S, Piecuch P, Kowalski K, Kucharski SA, Musial M. Where Does the Planar-to-Nonplanar Turnover Occur in Small Gold Clusters? *Journal of the American Chemical Society*. 2004; 127:1049–1052. [PubMed: 15656643]
 34. Humphrey W, Dalke A, Schulten K. VMD - Visual Molecular Dynamics. *J. Mol. Graphics*. 1996; 14:33–38.
 35. VMD User's Guide Version 1.9. University of Illinois at Urbana-Champaign; Urbana, IL: 2011.

36. Amin EA, Truhlar DG. Zn coordination chemistry: development of benchmark suites for geometries, dipole moments, and bond dissociation energies and their use to test and validate density functionals and molecular orbital theory. *J. Chem. Theory Comput.* 2008; 4:75–85.
37. Zhao Y, Truhlar DG. Benchmark databases for nonbonded interactions and their use to test density functional theory. *J. Chem. Theory Comput.* 2004; 1:415–432.
38. The higher-level calculations were only conducted on the cis configuration because of these results.
39. Jiménez-Hoyos CA, Janesko BG, Scuseria GE. Evaluation of Range-Separated Hybrid and Other Density Functional Approaches on Test Sets Relevant for Transition Metal-Based Homogeneous Catalysts†. *The Journal of Physical Chemistry A.* 2009; 113:11742–11749. [PubMed: 19585973]
40. Bühl M, Reimann C, Pantazis DA, Bredow T, Neese F. Geometries of Third-Row Transition-Metal Complexes from Density-Functional Theory. *Journal of Chemical Theory and Computation.* 2008; 4:1449–1459.
41. Feller D. The Role of Databases in Support of Computational Chemistry Calculations. *J. Comput. Chem.* 1996; 17:1571–1586.
42. Schuchardt KL, Didier BT, Elsethagen T, Sun L, Gurumoorthi V, Chase J, Li J, Windus TL. Basis Set Exchange: A Community Database for Computational Sciences. *J. Chem. Inf. Model.* 2007; 47:1045–1052. [PubMed: 17428029]

Highlights

ReOX_3 and ReOX_4^- ($X^- = \text{NH}_2^-$; OH^- ; PH_2^- ; SH^- ; Cl^- ; SeH^-) model systems investigated

PBE0 outperforms B3LYP in reproducing the MP2/ACPTZ results for the model complexes

PBE0/LTZ631** is reliable for computing the geometry of monooxorhenium(V) complexes

Selenium-containing complexes require a single-point energy calculation

Results compared with literature crystal structures

Fig. 1. MP2/ACPTZ equilibrium structures and point groups for the global minima of the model systems. Re: aqua; O: red; N: blue; P: orange; S: yellow; Cl: green; Se: gold; H: white.

Fig. 2.
PBE0/LTZ631** optimized structures for the five literature compounds. Re: aqua; O: red;
N: blue; P: orange; S: yellow; Cl: green; Se: gold; H: white.

Table 1

Basis set combinations employed in our calculations and their abbreviations^a

Basis Set Abbreviation	Basis Set and ECP for Re	Basis Set for all other Atoms
LDZ	LANL2DZ	LANL2DZ
SDD	SDD	SDD
LDZ631*	LANL2DZ	6-31G*
LDZ631**	LANL2DZ	6-31G**
LDZ631++*	LANL2DZ	6-31++G*
LDZ631+**	LANL2DZ	6-31+G**
LDZ631++**	LANL2DZ	6-31++G**
LDZ6311*	LANL2DZ	6-311G*
LDZ6311+*	LANL2DZ	6-311+G*
SDDMIDI	SDD	Midi! ^b
SDD6311*	SDD	6-311G*
SDD6311+*	SDD	6-311+G*
LTZ631*	LANL2TZ ^c	6-31G*
LTZ631**	LANL2TZ	6-31G**
LTZ631++*	LANL2TZ	6-31++G*
LTZ631+**	LANL2TZ	6-31+G**
LTZ631++**	LANL2TZ	6-31++G**
LTZ6311*	LANL2TZ	6-311G*
LTZ6311+*	LANL2TZ	6-311+G*
LTZf631*	LANL2TZ(f) ^c	6-31G*
LTZf631**	LANL2TZ(f)	6-31G**
LTZf631++*	LANL2TZ(f)	6-31++G*
LTZf631+**	LANL2TZ(f)	6-31+G**
LTZf631++**	LANL2TZ(f)	6-31++G**
LTZf6311*	LANL2TZ(f)	6-311G*
LTZf6311+*	LANL2TZ(f)	6-311+G*
ACPTZ	aug-cc-pVTZ-pp	aug-cc-pVTZ

^aMP2 method was not used in conjunction with the mixed LTZ or LTZf basis sets. The CCSD(T) method was only used in conjunction with the ACPTZ basis set.

^bMidi! is not available for P or Se.

^cThe LANL2TZ and LANL2TZ(f) ECP basis sets for rhenium were obtained from the EMSL Basis Set Exchange (<https://bse.pnl.gov/bse/portal>) [41, 42].

Table 2Additional basis sets employed for the selenium model system calculations^a

Basis Set Abbreviation	Basis Set and ECP for Re	Basis Set and ECP for Se	Basis Set for other Atoms
LDZ631*Se	LANL2DZ	LANL2DZ	6-31G*
LDZ631**Se	LANL2DZ	LANL2DZ	6-31G**
LDZ631++*Se	LANL2DZ	LANL2DZ	6-31++G*
LDZ631+**Se	LANL2DZ	LANL2DZ	6-31+G**
LDZ631+++*Se	LANL2DZ	LANL2DZ	6-31++G**
LDZ6311*Se	LANL2DZ	LANL2DZ	6-311G*
LDZ6311+*Se	LANL2DZ	LANL2DZ	6-311+G*
LTZ631*Se	LANL2TZ	LANL08 ^b	6-31G*
LTZ631**Se	LANL2TZ	LANL08	6-31G**
LTZ631++*Se	LANL2TZ	LANL08	6-31++G*
LTZ631+**Se	LANL2TZ	LANL08	6-31+G**
LTZ631+++*Se	LANL2TZ	LANL08	6-31++G**
LTZ6311*Se	LANL2TZ	LANL08	6-311G*
LTZ6311+*Se	LANL2TZ	LANL08	6-311+G*
LTZf631*Se	LANL2TZ(f)	LANL08d ^b	6-31G*
LTZf631**Se	LANL2TZ(f)	LANL08d	6-31G**
LTZf631++*Se	LANL2TZ(f)	LANL08d	6-31++G*
LTZf631+**Se	LANL2TZ(f)	LANL08d	6-31+G**
LTZf631+++*Se	LANL2TZ(f)	LANL08d	6-31++G**
LTZf6311*Se	LANL2TZ(f)	LANL08d	6-311G*
LTZf6311+*Se	LANL2TZ(f)	LANL08d	6-311+G*

^aMP2 method was not used in conjunction with the mixed LTZ or LTZf basis sets. The CCSD(T) method was only used in conjunction with the ACPTZ basis set.

^bThe LANL08 and LANL08d ECP basis sets for selenium were obtained from the EMSL Basis Set Exchange (<https://bse.pnl.gov/bse/portal>) [41, 42].

Table 3

CCSD(T)/ACPTZ T1 diagnostic values for the MP2/ACPTZ equilibrium geometries.

Model system	T1 diagnostic value
ReO(NH ₂) ₃	0.024
ReO(NH ₂) ₄ ¹⁻	0.022
ReO(OH) ₃	0.026
ReO(OH) ₄ ¹⁻	0.022
ReO(PH ₂) ₃	0.027
ReO(PH ₂) ₄ ¹⁻	0.023
ReO(SH) ₃	0.027
ReO(SH) ₄ ¹⁻	0.022
ReOCl ₃	0.022
ReOCl ₄ ¹⁻	0.021
ReO(SeH) ₃	0.022
ReO(SeH) ₄ ¹⁻	0.017

Table 4

The top 20 structural average autoscale intersystem values (AAIV) for the DFT method and basis set combinations for all of the model systems^{a,b}

Method	Basis Set	AAIV ReOX ₃	AAIV ReOX ₄ ¹⁻	Overall Rank
B3LYP	ACPTZ	-0.351	-0.500	14
PBE0	LDZ631+**	0.243	-0.872	17
	LDZ631++**	0.273	-0.816	18
	SDD6311*	0.026	-0.693	16
	SDD6311+*	0.018	-0.444	20
	LTZ631*	-0.147	-0.365	19
	LTZ631**	-0.355	-0.576	13
	LTZ631++*	-0.181	-0.813	11
	LTZ631+**	-0.342	-1.002	4
	LTZ631++**	-0.333	-0.991	5
	LTZ6311*	-0.436	-0.547	12
	LTZ6311+*	-0.419	-0.614	10
	LTZf631*	-0.225	-0.524	15
	LTZf631**	-0.430	-0.727	7
	LTZf631++*	-0.268	-0.940	6
	LTZf631+**	-0.425	-0.994	3
	LTZf631++**	-0.419	-1.043	2
	LTZf6311*	-0.489	-0.630	9
	LTZf6311+*	-0.493	-0.685	8
	ACPTZ	-1.005	-1.475	1

^aThe DFT results were benchmarked against the MP2/ACPTZ results.

^bSelenium geometry optimizations were included in this data set, but the basis sets employed only for selenium were not included in either the autoscaling calculations or the overall rank.

Table 5

The top 10 DFT RMSD values for the selenium model systems and their relative rank^{a,b}

Method	Basis Set	RMSD ReO(SeH) ₃	Rank ReO(SeH) ₃	RMSD ReO(SeH) ₄ ¹⁻	Rank ReO(SeH) ₄ ¹⁻
PBE0	LDZ631**	0.0986	(45)	0.0334	6 (6)
	L TZ631*	0.0884	(27)	0.0348	10 (10)
	L TZ631**	0.0849	10 (15)	0.0312	2 (2)
	L TZ631+***	0.0865	(21)	0.0338	8 (8)
	L TZ631+***	0.0868	(22)	0.0328	5 (5)
	L TZf631*	0.0850	(16)	0.0347	9 (9)
	L TZf631**	0.0815	4 (8)	0.0301	1 (1)
	L TZf631+***	0.0828	5 (9)	0.0334	6 (6)
	L TZf631+***	0.0835	7 (11)	0.0326	4 (4)
	L TZf6311*	0.0797	2 (6)	0.0408	(19)
	L TZf6311+*	0.0803	3 (7)	0.0417	(21)
	L TZf631**Se	0.0838	9 (13)	0.0469	(27)
	L TZf6311*Se	0.0830	6 (10)	0.0478	(29)
	L TZf6311+*Se	0.0836	8 (12)	0.0477	(28)
	ACPTZ	0.0680	1 (1)	0.0318	3 (3)

^aThe DFT results were benchmarked against the MP2/ACPTZ results.

^bThe top 10 ranks based only on the DFT results are listed within their respective groups. The rank based on all of the method and basis set combinations used is in parentheses.

Table 6

The top 20 DFT average autoscale intersystem values for the complexation reactions (AAIVCR) for the model systems and their overall rank^{a,b}

Method	Basin Set	AAIVCR ΔE	AAIVCR ΔH°	AAIVCR ΔG°	Overall Rank ^b
B3LYP	LDZ631**	-0.103	-0.123	-0.154	19
	LDZ631+*	-0.101	0.378	0.412	20
	LDZ631+*	-0.245	0.099	0.119	15
	SDD631+*	-0.235	0.119	0.142	16
	LZT631+*	-0.213	0.141	0.163	18
	LZT631+*	-0.224	0.130	0.152	17
PBE0	LDZ631+*	-0.469	-0.509	-0.516	5
	LDZ631+*	-0.453	-0.482	-0.488	8
	LDZ631+*	-0.456	-0.482	-0.488	7
	LDZ631+*	-0.549	-0.701	-0.722	1
	SDD631+*	-0.519	-0.654	-0.668	3
	LZT631+*	-0.439	-0.483	-0.486	11
	LZT631+*	-0.432	-0.461	-0.466	13
	LZT631+*	-0.435	-0.464	-0.467	12
	LZT631+*	-0.514	-0.655	-0.674	4
	LZT631+*	-0.464	-0.508	-0.512	6
	LZT631+*	-0.443	-0.474	-0.476	10
	LZT631+*	-0.446	-0.477	-0.478	9
	LZT631+*	-0.547	-0.689	-0.707	2
	ACPTZ	-0.391	-0.476	-0.479	14

^cThe ranks displayed in this table are based on the AAIVCR ΔE for the DFT results only.

^dThe DFT results were benchmarked against the CCSD(T)/ACPTZ//MP2/ACPTZ results.

^eSelenium complexation energies were not included in this data set.

Table 7

Selenium model system complexation reaction unsigned errors: difference between the top 10 DFT/basis set combinations and CCSD(T)/ACPTZ//MP2/ACPTZ^a

Method	Basis Set	$\Delta\Delta E$	$\Delta\Delta H^\circ$	$\Delta\Delta G^\circ$	Rank ^b
B3LYP	LDZ	2.4	2.5	2.2	1
	LDZ631**Se	3.0	3.1	2.8	9
	LDZ631++*Se	2.8	2.9	2.6	4
	LDZ631+**Se	2.9	3.1	2.8	8
	LDZ631++**Se	2.5	2.7	2.4	2
	LDZ6311*Se	2.8	3.0	2.7	4
	LDZ6311+*Se	3.1	3.1	2.9	10
PBE0	LTZ631*Se	2.8	2.6	2.8	4
	LTZ631**Se	2.8	2.7	2.9	4
	LTZ6311*Se	2.7	2.6	2.8	3

^aEnergy differences in kcal/mol.

^bThe ranks displayed in this table are based on the $\Delta\Delta E$ for the DFT results only.

Table 8

Comparison of mean unsigned errors in complexation energies from single-point energy calculations to CCSD(T)/ACPTZ//MP2/ACPTZ results^a

Optimization Method/Basis Set	Single-point energy Method/Basis Set	$\Delta\Delta E_{\text{MUE}}$	$\Delta\Delta H^{\circ}_{\text{MUE}}$	$\Delta\Delta G^{\circ}_{\text{MUE}}$
PBE0/LTZ631**	PBE0/LTZ631**	8.6	7.8	7.7
PBE0/LTZ631**	PBE0/LDZ6311*	10.9	10.9	10.9
	PBE0/LDZ6311*Se	11.3	11.3	11.4
	PBE0/LDZ6311+*	4.3	4.2	4.2
	PBE0/LDZ6311+*Se	3.5	3.5	3.5
	PBE0/SDD6311+*	4.5	4.4	4.4
	PBE0/LTZ6311*	10.8	10.8	10.7
	PBE0/LTZ6311*Se	10.4	10.4	10.4
	PBE0/LTZ6311+*	4.5	4.5	4.4
	PBE0/LTZ6311+*Se	3.6	3.5	3.5
	PBE0/LTZf6311*	10.4	10.4	10.3
	PBE0/LTZf6311*Se	11.0	11.0	10.8
	PBE0/LTZf6311+*	4.1	4.1	4.0
	PBE0/LTZf6311+*Se	4.0	3.9	3.8
MP2/ACPTZ	CCSD(T)/ACPTZ	0.0	0.0	0.0

^a All mean unsigned errors in kcal/mol.

Table 9

Autoscale RMSD values (equation 1) and the average autoscaled intersystem values ($AAIV_{LIT}$, equation 2) for the literature compounds

Method	Basis set	Autoscale _{L1}	Autoscale _{L2}	Autoscale _{L3}	Autoscale _{L4}	Autoscale _{L5}	$AAIV_{LIT}$	Rank
B3LYP	LDZ631*	0.939023667	0.089538199	0.119045757	-0.457187442	1.337182971	0.40552063	22
	LDZ631**	0.383584322	0.089538199	0.098936417	-0.621017139	1.1135938	0.21292712	16
	LDZ631++*	0.558861882	1.728654872	2.02715744	0.320227419	1.537350657	1.234450454	30
	LDZ631+++	-0.154909319	1.547741084	1.749522589	0.377201495	1.205143924	0.944939955	28
	LDZ631++**	0.103969221	1.645756411	1.739574217	0.342938404	1.246932937	1.015834238	29
	LTZ631*	0.003026043	0.935939108	-0.1460707	1.190373861	0.637656738	0.52418501	26
	LTZ631**	-0.51187246	0.875027239	-0.309171388	1.14300036	0.328753302	0.305147411	21
	LTZ631+*	-0.55307995	1.146059523	0.747979847	0.90669345	1.12481021	0.674492616	27
	LTZ631+++	-1.180468846	1.123960569	0.579150565	1.089615512	0.816445576	0.485740675	24
	LTZ631++**	-1.076384783	1.064172518	0.507907591	1.127280621	0.920601439	0.508715477	25
PBE0	LDZ631*	-0.592942952	0.151369006	0.243905933	1.350763433	0.262694078	0.2831579	20
	LDZ631**	-1.043376357	0.095658165	0.07066747	1.269825942	0.034550784	0.085465201	15
	LDZ631++*	-1.27920281	0.35532166	1.08540109	1.15436234	0.736346694	0.410445795	23
	LDZ631+++	-1.869473569	0.33499282	0.877266534	1.192082516	0.563988501	0.21977136	18
	LDZ631++**	-1.764276291	0.261480872	0.836043693	1.185355404	0.569044032	0.217529542	17
	LDZ631*	2.085252225	-1.791513225	-1.327170825	-1.882824199	0.21752765	-0.539745675	8
	LDZ631**	1.692297683	-1.855853364	-1.463789819	-2.042309547	0.032713248	-0.72738836	6
	LDZ631+*	1.726428058	0.236281449	0.729050926	-1.299872323	-0.020094014	0.274358819	19
	LDZ631+++	0.948554687	0.078040358	0.305305411	-1.261798452	-0.46562852	-0.079105303	13
	LDZ631++**	1.256388799	0.153899728	0.274630598	-1.348261045	-0.246581762	0.018015264	14
	LTZ631*	0.80738375	-0.571061489	-1.436406408	-0.456946837	-1.415210697	-0.614448336	7
	LTZ631**	0.26382506	-0.5658638	-1.755779139	-0.580478548	-1.5860577	-0.844870825	2
	LTZ631+*	0.467670966	-0.30787404	-0.441609849	-0.525132987	-0.571104551	-0.275610092	12
	LTZ631+++	-0.081558122	-0.369777363	-0.699395101	-0.49260948	-1.02449377	-0.535566767	9
	LTZ631++**	0.05392201	-0.371392292	-0.840280364	-0.530591694	-0.837075015	-0.505083471	10
	LTZ631*	0.399387753	-1.327932031	-1.073804493	-0.120273433	-1.571230379	-0.738770517	4
	LTZ631**	0.011935115	-1.338824475	-1.418837516	-0.216644615	-1.837554811	-0.95998526	1

Method	Basis set	Autoscale _{L1}	Autoscale _{L2}	Autoscale _{L3}	Autoscale _{L4}	Autoscale _{L5}	AAIV _{Lit}	Rank
	LTZF631++*	-0.18096505	-1.067780067	-0.103543037	-0.2791408	-0.853864778	-0.497058747	11
	LTZF631+**	-0.771116518	-1.169738706	-0.435607811	-0.269850729	-1.20387402	-0.770037557	3
	LTZF631+++	-0.641884217	-1.175820927	-0.540079627	-0.264781488	-1.052566528	-0.735026557	5

^aThe DFT structures were benchmarked against the reported crystal structures [13-16].