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Title: Estimation of $\Delta R/R$ Values by Benchmark Study of the Mössbauer Isomer Shifts for Ru, Os complexes Using Relativistic DFT Calculations

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Abstract:

The present study applies all-electron relativistic DFT calculation with Douglas-Kroll-Hess (DKH) Hamiltonian to each ten sets of Ru and Os compounds. We perform the benchmark investigation of three density functionals (BP86, B3LYP and B2PLYP) using segmented all-electron relativistically contracted (SARC) basis set with the experimental Mössbauer isomer shifts for ⁹⁹Ru and ¹⁸⁹Os nuclides. Geometry optimizations at BP86 theory of level locate the structure in a local minimum. We calculate the contact density to the wavefunction obtained by a single point calculation. All functionals show the good linear correlation with experimental isomer shifts for both ⁹⁹Ru and ¹⁸⁹Os. Especially, B3LYP functional gives a stronger correlation compared to BP86 and B2PLYP functionals. The comparison of contact density between SARC and well-tempered basis set (WTBS) indicated that the numerical convergence of contact density cannot be obtained, but the reproducibility is less sensitive to the choice of basis set. We also estimate the values of $\Delta R/R$, which is an important nuclear constant, for ⁹⁹Ru and ¹⁸⁹Os nuclides by using the benchmark results. The sign of the calculated $\Delta R/R$ values is consistent with the predicted data for ⁹⁹Ru and ¹⁸⁹Os. We obtain computationally the $\Delta R/R$ values of ⁹⁹Ru and ¹⁸⁹Os (36.2 keV) as 2.35×10^{-4} and -0.20×10^{-4} , respectively, at B3LYP level for SARC basis set.

Keywords: Mössbauer isomer shift; Density functional theory; Benchmark study; $\Delta R/R$

Text:

1 Introduction

The bonding study between a metal and ligands on transition metal complexes is desired in order to estimate their stability and reactivity. Mössbauer spectroscopy enables us to observe an electronic state of the atom to which the Mössbauer nucleus belongs [1]. Especially, Mössbauer isomer shifts (δ) describe not only the oxidation and the spin states of Mössbauer elements, but also the bonding properties quantitatively. δ is formulated as the difference between electron densities at nuclear position, i.e. contact density (ρ_0), of absorber (ρ_0^{absorber}) and source (ρ_0^{source}) multiplied by the constant coefficient depending on only Mössbauer nuclides (Eq. 1):

$$\delta = \{(4\pi/5) Ze^2R^2 (\Delta R/R)\} (\rho_0^{\text{absorber}} - \rho_0^{\text{source}}) \quad (1)$$

where e is the elementary electric charge, Z and R are the nuclear charge and its radius, respectively, and ΔR is the variation of the nuclear radius between Mössbauer transition states [1]. We can obtain ρ_0 values by a quantum chemical calculation and connect the theoretical calculation with the Mössbauer isomer shifts (Eq. 2) [2].

$$\delta^{\text{exp}} = a (\rho_0^{\text{calc}} - b) \quad (2)$$

The linear relationship between the experimental Mössbauer isomer shifts (δ^{exp}) and the calculated ρ_0 values (ρ_0^{calc}) enables us to evaluate the performance of a computational method. We can also estimate the $\Delta R/R$ value of a Mössbauer transition by comparing between Eq. 1 and the calibration constant (a) in Eq. 2 obtained by benchmarking [2].

We have performed the benchmark study on relativistic DFT calculation for lanthanide and actinide compounds by referring to the experimental data of ^{151}Eu and ^{237}Np Mössbauer isomer shifts [3]. We have also indicated the application possibility of DFT to the task for minor-actinides separation from lanthanides, leading to solving the disposal of high-level liquid waste [4]. The present study aims to estimate the DFT performance for Ru and Os compounds by the benchmarking with the experimental Mössbauer isomer shifts of ^{99}Ru and ^{189}Os systems. The benchmark study with Mössbauer isomer shifts has been performed energetically for ^{57}Fe system [5-9]. However, it has been hardly done for ^{99}Ru and ^{189}Os systems. Furthermore, the estimation of $\Delta R/R$ values is first demonstrated by combining δ with DFT calculations for Ru and Os complexes, since the negative sign of the $\Delta R/R$ value for ^{189}Os (36.2 keV) observed experimentally was reported by combining δ with the only use of self-consistent field

calculations for free ions.

2 Computational details

All DFT calculations were performed by using ORCA ver. 3.0 [10]. The computation of ρ_0 values requires unconditionally a set of all-electron basis function for a Mössbauer atom. The relativistic Hamiltonian needs to be included in the Kohn-Sham equation in order to consider the relativistic effect of a heavy atom. Scalar-relativistic second-order Douglas-Kroll-Hess (DKH2) procedure [11] was introduced into the Hamiltonian with a finite nucleus model as uniformly charged sphere [12] to avoid the divergence of the s-electron density at nucleus position in the case of a scalar-relativistic calculation using a point charged nucleus [13-14]. Spin-orbit coupling effect was considered by using the Breit-Pauli perturbative method. Segmented all-electron relativistic contracted (SARC) basis sets optimized for DKH2 calculation were assigned to all atoms. The SARC basis set for Os atom was referred to Ref. 15. For the other atoms, we used the recontracted version implemented in ORCA: the exponents are cited in Ref. 16 and the method of recontraction can be obtained in Ref.15. The basis sets of Ru and Os atoms were assigned as (19s14p9d) contracted to (12s9p5d) with one p-type polarization function and (22s15p11d5f) contracted to (17s11p8d2f) with one f-type polarization function, respectively, for both geometry optimizations and single-point calculations. Geometry optimizations were performed without any geometrical constraints at a BP86 / SVP (SARC-DKH) theory of level. All single-point energies were obtained by three functionals, including BP86, B3LYP and B2PLYP functionals, with TZVP (SARC-DKH) basis sets. The resolution of the identity (RI) approximation was employed for all self-consistent field (SCF) calculations in a pure-DFT calculation with Split-RI-J [17]; in a hybrid-DFT calculation with RIJCOSX [18]. The accuracy and grid parameters for SCF calculations were employed with the same setting to our previous work [3].

Each ten complexes for Ru and Os systems in which the experimental Mössbauer isomer shifts were available were chosen for the benchmarking shown in Table 1. We employed the experimental isomer shifts measured at 4.2 K. The geometries for $[M(\eta^5\text{-C}_5\text{H}_5)_2]$ ($M = \text{Ru}^{\text{II}}, \text{Os}^{\text{II}}$) [19-20] and $[M(\text{bipy})_3]$ ($M = \text{Ru}^{\text{III}}, \text{Os}^{\text{II}}$; bipy = 2,2'-bipyridine) [21-22] were referred to single crystal X-ray structures as the starting coordinates when optimized. We constructed the starting geometries for four-, five- and six-coordinated compounds as tetrahedral, trigonal bipyramidal and octahedral systems, respectively. We regarded the spin state which has the lowest energy among different spin states as their electronic ground states (Table 1).

3 Results and discussion

All equilibrium geometries were obtained in local minima. Tables 2 and 3 show the ρ_0^{calc} values obtained by single-point calculations employing each method for Ru and Os complexes, respectively. As shown in Figure 1, very high linear correlations between δ^{exp} and ρ_0^{calc} were obtained with the coefficients of determination (R^2) whose values are higher than 0.88 for all systems. The standard deviation values for Ru and Os systems decrease in order of BP86, B2PLYP and B3LYP. In the cases for both ^{99}Ru and ^{189}Os , we found that B3LYP functional gives the stronger correlation with experimental isomer shifts compared to BP86 and B2PLYP functionals. Our previous benchmark results with ^{151}Eu and ^{237}Np Mössbauer isomer shifts showed the slightly different tendency that B2PLYP is more suitable for the evaluation of bonding nature in f-block complexes compared to BP86 and B3LYP. The bonding nature in compounds depends on the exchange interaction between two electrons. The mixing ratio of exchange term in exchange-correlation potential between Hartree-Fock and DFT is different among three functionals. BP86, B3LYP and B2PLYP contain 0, 20 and 53 % of Hartree-Fock exchange admixture, respectively. It is implied that the more suitable mixing ratio of Hartree-Fock exchange term to evaluate the bonding interaction between metal and ligands is different between d- and f-metal ions, although it should be discussed carefully in future work. We, however, indicate that hybrid DFT, such as B3LYP or B2PLYP, is proper methods which reproduces the bonding properties for both d- and f-block compounds compared to pure DFT, such as BP86. It is suggested that the benchmarking of DFT with Mössbauer isomer shifts enables us to evaluate the validity of the bonding property for a heavy metal ion, such as 5d and 5f metal ions.

We also checked the validity of the SARC basis sets for Ru and Os atoms. We performed the single-point calculations for the smaller sets of Ru and Os complexes to obtain their calculated ρ_0 values using Huzinaga's well-tempered basis set (WTBS) in completely uncontracted form (28s20p17d) for Ru atom and (32s23p18d12f) for Os atom [26-27]. Table 4 shows the comparison of the ρ_0^{calc} values and the R^2 values between SARC and uncontracted WTBS (unc WTBS) at DKH2-BP86 level of theory for Ru and Os complexes. The absolute values of ρ_0^{calc} values in the case of SARC basis set were very smaller than those in the case of unc WTBS by the percentage of 66.6 and 58.6 % for Ru and Os systems, respectively. This failure to numerically converge might be based on the lack of the steepness of s-type GTO basis functions in core region for SARC basis set compared to that for WTBS, not the divergence of wavefunction when approaching a point nucleus, because our calculations include the finite nucleus approximation.

However, what we need is not the absolute value of contact density, but variations of the contact density. When focusing on the linearity between Mössbauer isomer shifts and ρ_0^{calc} value, the correlation coefficient (R) is improved for Ru system and almost unchanged for Os system by changing the basis set from unc WTBS to SARC. The resulting standard deviation indicated that SARC basis set have the reproducibility of Mössbauer isomer shifts as equal to unc WTBS. This implies that the variation of contact density is less sensitive to the effect of very tight primitive functions of basis set than the value of the ρ_0 value itself as Kurian and Filatov reported [28]. The slope value in Table 4, however, varies depending on basis set. Their absolute values for SARC are larger than those for WTBS by 36 and 65 % for ^{99}Ru and ^{189}Os systems, respectively. This indicated that the variation of the ρ_0^{calc} value for SARC basis set is more sensitive to the oxidation states for Ru and Os atoms than that for WTBS due to the effect of the convergence of basis set. The amount of change from minimum to maximum values of ρ_0^{calc} was 21.7 / 26.1 a.u.⁻³ for SARC / WTBS in the case of ^{99}Ru system, and 87.2 / 142.9 a.u.⁻³ for SARC / WTBS in the case of ^{189}Os system. This indicated that the result of SARC underestimates the variation of contact density compared to that of WTBS. This underestimation might be caused by that the failure of convergence of contact density makes the response to the change of valence state weaker.

We calculated the $\Delta R/R$ values by substituting their calibration constant for a in a following equation (Eq. 3):

$$(\Delta R/R) = a (5\varepsilon_0 E_\gamma) / (3Ze^2 c R^2) \quad (3)$$

where E_γ is the γ -ray transition energy of Mössbauer level, c is the speed of light. The nucleus radius (R) was approximated as $1.2 A^{1/3}$ fm, where A is the mass number of Mössbauer nucleus. Table 5 shows the $\Delta R/R$ values calculated by using Eq. 3. We obtained the sign of calculated $\Delta R/R$ values as positive for ^{99}Ru . This result is consistent with the experimental sign of $\Delta\langle r^2 \rangle / \langle r^2 \rangle$ [2], although the absolute value for ^{99}Ru ($\Delta\langle r^2 \rangle / \langle r^2 \rangle = 28$) does not correlate to experimental value. The calculated $\Delta R/R$ value of 36.2 keV for ^{189}Os has a negative sign. Our result correlates to the result estimated by the Dirac-Fock calculation to Os free ions in which the sign of $\Delta\langle r^2 \rangle$ for ^{189}Os (36.2 keV) was negative ($\Delta\langle r^2 \rangle = -2.0 \times 10^{-3}$ fm²) [25]. This reported value did not consider the ligands surrounding a metal ion, but our present value first contains the contribution of the ligands in all-electron relativistic SCF calculations. Compared the calculated $\Delta R/R$ values for SARC basis set, all values are consistent within their standard deviations. The calculated $\Delta R/R$ values are $2.35 \sim 2.74 \times 10^{-4}$ for ^{99}Ru and $-0.22 \sim -0.20 \times 10^{-4}$ for ^{189}Os

(36.2 keV). The comparison of $\Delta R/R$ values between SARC and WTBS basis sets for BP86 functional indicated that its absolute value for SARC is larger than that for WTBS for both ^{99}Ru and ^{189}Os systems. This overestimation can be related to the overestimation of the response to the change of valence state as mentioned above. We expect that these discussions lead to the accurate estimation of $\Delta R/R$ values as well as the improvement of DFT calculations by benchmarking.

4 Conclusion

We applied all-electron relativistic DFT calculation to Ru and Os complexes. The calculated electron densities at the nucleus position in their compounds strongly correlated to the corresponding Mössbauer isomer shifts of ^{99}Ru and ^{189}Os nuclei. The linear relationship between the experimental isomer shifts and the calculated ρ_0 values enabled us to evaluate the validity of computational method for the bonding properties. We first performed the benchmark study of relativistic DFT computation with ^{99}Ru and ^{189}Os isomer shifts to indicate that B3LYP functional reproduces experimental results with the higher correlation than BP86 and B2PLYP methods. We also estimated the $\Delta R/R$ values by the calibration constant (a) for ^{99}Ru and ^{189}Os nuclides. The sign of the calculated $\Delta R/R$ values was consistent with the experimental results for ^{99}Ru [24] and ^{189}Os (36.2 keV) [25]. We checked the reproducibility of SARC basis set by comparing the ρ_0^{calc} values with uncontracted WTBS basis set for BP86 functional and also indicated that the numerical convergence of contact density relates to the responsibility to the change of valence electron state. This work reveals that the benchmarking with the Mössbauer isomer shifts is a powerful methodology not only to predict the bonding states, especially, for heavier atoms, but also to estimate the important nuclear parameter, $\Delta R/R$, even if the value is not obtained experimentally.

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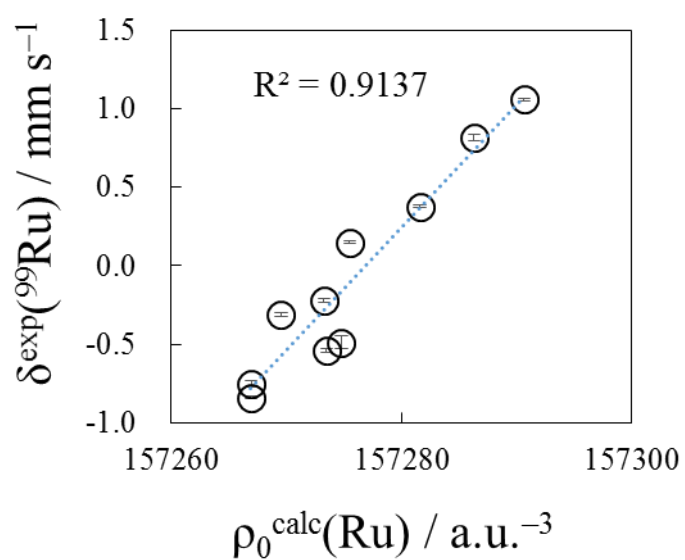
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(a) ^{99}Ru



(b) ^{189}Os (36.2 keV)

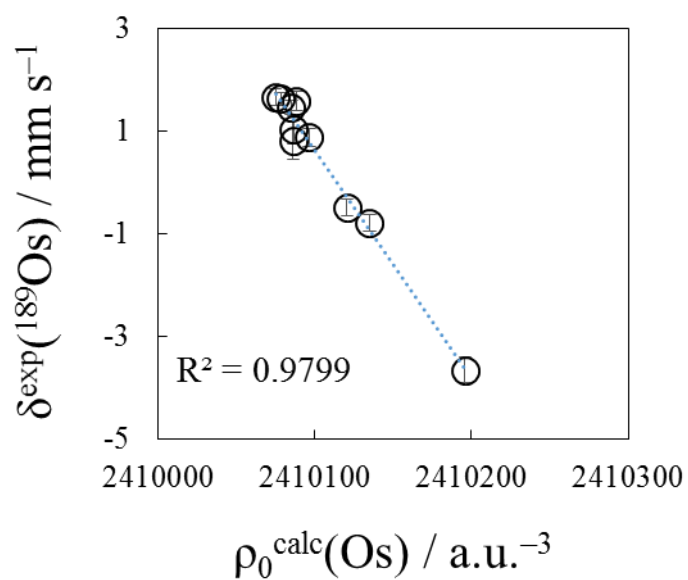


Fig. 1 The benchmark plots between the experimental isomer shifts and the calculated electron densities at nucleus position at B3LYP for (a) ^{99}Ru and (b) ^{189}Os .

Table 1 Benchmark complexes for Ru and Os systems

Ru complexes	S	$\delta_{\text{Ru}}^{\text{exp}}$ / mms^{-1} ^a	Os complexes	S	$\delta_{\text{Os}}^{\text{exp}}$ / mms^{-1} ^d
$[\text{Ru}^{\text{II}}(\text{C}_5\text{H}_5)_2]^0$	0	$-0.75(2)^b$	$[\text{Os}^{\text{II}}(\text{C}_5\text{H}_5)_2]^0$	0	$1.67(16)^e$
$[\text{Ru}^{\text{II}}(\text{CN})_6]^{4-}$	0	$-0.22(1)^b$	$[\text{Os}^{\text{II}}(\text{bipy})_3]^{2+}$	0	$1.47(14)^e$
$[\text{Ru}^{\text{III}}(\text{NCS})_6]^{3-}$	1/2	$-0.49(4)^b$	$[\text{Os}^{\text{II}}(\text{CN})_6]^{4-}$	0	$0.89(17)^e$
$[\text{Ru}^{\text{III}}\text{F}_6]^{3-}$	1/2	$-0.84(1)^c$	$[\text{Os}^{\text{III}}(\text{NCS})_6]^{3-}$	1/2	$1.59(19)^e$
$[\text{Ru}^{\text{III}}(\text{bipy})_3]^{3+}$	1/2	$-0.54(1)^b$	$[\text{Os}^{\text{IV}}\text{F}_6]^{2-}$	1	$1.64(13)^e$
$[\text{Ru}^{\text{IV}}\text{Cl}_6]^{2-}$	0	$-0.31(1)^c$	$[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$	1	$1.04(27)^e$
$[\text{Ru}^{\text{V}}\text{F}_5]^0$	0	$0.15(1)^c$	$[\text{Os}^{\text{IV}}\text{Br}_6]^{2-}$	1	$0.83(37)^e$
$[\text{Ru}^{\text{VI}}\text{O}_4]^{2-}$	1	$0.38(1)^b$	$[\text{Os}^{\text{VI}}\text{Cl}_5\text{N}]^{2-}$	0	$-0.47(16)^e$
$[\text{Ru}^{\text{VII}}\text{O}_4]^-$	1/2	$0.82(2)^b$	$[\text{Os}^{\text{VI}}\text{F}_6]^0$	1	$-0.78(16)^e$
$[\text{Ru}^{\text{VIII}}\text{O}_4]^0$	0	$1.06(1)^b$	$[\text{Os}^{\text{VIII}}\text{O}_4]^0$	0	$-3.64(24)^e$

^aRelative values to metal Ru at 4.2 K.

^bReference 23.

^cReference 24.

^dRelative values to ^{189}Ir source for 36.2 keV transition at 4.2 K.

^eReference 25.

Table 2 Calculated electron densities at Ru nucleus position and linear regression parameters at three functionals

Ru complexes	$\delta_{\text{Ru}}^{\text{exp}}$ / mms^{-1}	BP86		B3LYP		B2PLYP	
		ρ_0^{calc} / a.u.^{-3}	$\delta_{\text{Ru}}^{\text{calc}}$ / mms^{-1}	ρ_0^{calc} / a.u.^{-3}	$\delta_{\text{Ru}}^{\text{calc}}$ / mms^{-1}	ρ_0^{calc} / a.u.^{-3}	$\delta_{\text{Ru}}^{\text{calc}}$ / mms^{-1}
[Ru ^{II} (C ₅ H ₅) ₂]	-0.75	157419.773	-0.74	157266.955	-0.78	157201.985	-0.81
[Ru ^{II} (CN) ₆] ⁴⁻	-0.22	157426.110	-0.20	157273.285	-0.28	157208.345	-0.23
[Ru ^{III} (NCS) ₆] ³⁻	-0.49	157427.302	-0.10	157274.799	-0.16	157209.727	-0.10
[Ru ^{III} F ₆] ³⁻	-0.84	157419.203	-0.79	157266.920	-0.78	157201.566	-0.85
[Ru ^{III} (bipy) ₃] ³⁺	-0.54	157426.006	-0.21	157273.512	-0.26	157208.480	-0.22
[Ru ^{IV} Cl ₆] ²⁻	-0.31	157421.353	-0.61	157269.572	-0.57	157204.469	-0.58
[Ru ^V F ₅]	0.15	157426.331	-0.19	157275.520	-0.11	157210.180	-0.06
[Ru ^{VI} O ₄] ²⁻	0.38	157432.435	0.34	157281.616	0.37	157215.013	0.38
[Ru ^{VII} O ₄] ⁻	0.82	157436.892	0.72	157286.342	0.74	157218.816	0.73
[Ru ^{VIII} O ₄]	1.06	157440.928	1.06	157290.656	1.08	157221.897	1.01
a / mms^{-1} a.u.^3		0.085		0.078		0.091	
b / a.u.^{-3}		157428.501		157276.863		157210.858	
Correlation coefficient (R)		0.936		0.956		0.948	
standard deviation / mms^{-1}		0.22		0.18		0.20	

Table 3 Calculated electron densities at Os nucleus position and linear regression parameters at three functionals

Os complexes	$\delta_{\text{Os}}^{\text{exp}}$ / mms^{-1}	BP86		B3LYP		B2PLYP	
		ρ_0^{calc} / a.u.^{-3}	$\delta_{\text{Os}}^{\text{calc}}$ / mms^{-1}	ρ_0^{calc} / a.u.^{-3}	$\delta_{\text{Os}}^{\text{calc}}$ / mms^{-1}	ρ_0^{calc} / a.u.^{-3}	$\delta_{\text{Os}}^{\text{calc}}$ / mms^{-1}
[Os ^{II} (C ₅ H ₅) ₂]	1.67	2412930.999	1.70	2410074.963	1.74	2407833.836	1.75
[Os ^{II} (bipy) ₃] ²⁺	1.47	2412943.551	1.09	2410084.946	1.30	2407845.306	1.19
[Os ^{II} (CN) ₆] ⁴⁻	0.89	2412952.424	0.65	2410096.410	0.79	2407855.019	0.73
[Os ^{III} (NCS) ₆] ³⁻	1.59	2412943.459	1.09	2410088.277	1.15	2407846.639	1.13
[Os ^{IV} F ₆] ²⁻	1.64	2412930.947	1.71	2410078.311	1.59	2407835.547	1.67
[Os ^{IV} Cl ₆] ²⁻	1.04	2412938.405	1.34	2410086.294	1.24	2407843.508	1.28
[Os ^{IV} Br ₆] ²⁻	0.83	2412938.658	1.33	2410086.265	1.24	2407843.094	1.30
[Os ^{VI} Cl ₅ N] ²⁻	-0.47	2412972.043	-0.31	2410120.516	-0.28	2407874.720	-0.22
[Os ^{VI} F ₆]	-0.78	2412980.938	-0.74	2410134.953	-0.92	2407891.699	-1.04
[Os ^{VIII} O ₄]	-3.64	2413039.665	-3.63	2410195.843	-3.62	2407943.425	-3.54
a / mms^{-1} a.u.^3		-0.049		-0.044		-0.048	
b / a.u.^{-3}		2412965.753		2410114.238		2407870.067	
Correlation coefficient (R)		-0.983		-0.990		-0.985	
standard deviation / mms^{-1}		0.29		0.22		0.27	

Table 4 Comparison of the calculated electron densities at nucleus position (ρ_0^{calc}) for Ru and Os atoms between SARC and uncontracted WTBS (unc WTBS) for BP86 functional

Ru complexes	$\delta_{\text{Ru}}^{\text{exp}}$ / mms ⁻¹	$\rho_0^{\text{calc}}(\text{Ru}) / \text{a.u.}^{-3}$		Os complexes	$\delta_{\text{Os}}^{\text{exp}}$ / mms ⁻¹	$\rho_0^{\text{calc}}(\text{Os}) / \text{a.u.}^{-3}$	
		SARC	unc WTBS			SARC	unc WTBS
[Ru ^{II} (CN) ₆] ²⁻	-0.22	157426.110	236296.842	[Os ^{II} (CN) ₆] ²⁻	0.89	2412952.424	4116318.151
[Ru ^{III} F ₆] ³⁻	-0.84	157419.203	236295.368	[Os ^{III} (NCS) ₆] ³⁻	1.59	2412943.459	4116297.868
[Ru ^{VI} O ₄] ²⁻	0.38	157432.435	236310.038	[Os ^{IV} F ₆] ²⁻	1.64	2412930.947	4116279.154
[Ru ^{VII} O ₄] ⁻	0.82	157436.892	236315.121	[Os ^{VI} F ₆]	-0.78	2412980.938	4116362.910
[Ru ^{VIII} O ₄]	1.06	157440.928	236321.449	[Os ^{VIII} O ₄]	-3.64	2413039.665	4116461.014
<i>a</i> / mms ⁻¹ a.u. ³		0.090	0.066	<i>a</i> / mms ⁻¹ a.u. ³		-0.051	-0.031
<i>b</i> / a.u. ⁻³		157428.437	236304.120	<i>b</i> / a.u. ⁻³		2412963.313	4116341.857
Correlation coefficient (<i>R</i>)		0.998	0.968	Correlation coefficient (<i>R</i>)		-0.995	-0.995
standard deviation / mms ⁻¹		0.04	0.18	standard deviation / mms ⁻¹		0.20	0.19

Table 5 Comparison of calculated $\Delta R/R$ values for SARC and WTBS basis sets

Mössbauer Nuclide	E_γ / keV	$(\Delta R/R) / 10^{-4}$			
		SARC*			unc-WTBS**
		BP86	B3LYP	B2PLYP	BP86
^{99}Ru	89.4	2.56(34)	2.35(26)	2.74(32)	1.98(30)
^{189}Os	36.2	-0.225(15)	-0.203(10)	-0.221(14)	-0.140(8)

*Estimated based on a values given in Tables 2 and 3.

**Estimated based on a values given in Table 4.