

ARE OCTAHEDRAL RUTHENIUM(II/III) AND OSMIUM(II/III) COMPLEXES ALWAYS LOW-SPIN?

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Dedicated to Professor Rudolf Zahradník on the occasion of his 80th birthday.

The influence of geometrical changes on the spin multiplicity of the ground states of the octahedral ruthenium(II/III) and osmium(II/III) complexes is investigated using the TD-DFT and MRCI methods. On the example of the $[\text{RuCl}_6]^{4-}$ complex, we show that only after the optimisation of the molecular geometry in a solvent (using a polarised continuum model), which shortens the M-L bond lengths by ~ 0.2 Å, is the correct order of spin states obtained (i.e. a singlet is correctly predicted to be the ground state). On the contrary, in terms of the *in vacuo* optimised geometries of this negatively charged species, both the DFT and MRCI calculations predict a quintet ground state. This finding is further analysed by calculating the low- and high-spin potential energy curves corresponding to an elongation of the M-L distance, which makes it possible to predict the critical point at which the crossing of the two spin states occurs. Finally, it is complemented by the TD-DFT calculations of the lowest excited states in each spin multiplicity for a series of prototypical ligands. It is demonstrated that the calculated results correlate well with the known strengths of the ligand field. The two findings presented in this work are a small contribution to our understanding of the electronic structure and properties of the octahedral ruthenium(II/III) and osmium(II/III) complexes, which are relevant both in biomolecular and material sciences.

Keywords: Ruthenium complexes; Osmium; Spin state; Electronic spectra; Spin-orbit coupling; Solvatochromism; Spin density; DFT calculations; MRCI.

The octahedral complexes of ruthenium and osmium in their common oxidation states (II/III) have been the subject of many theoretical and experimental investigations¹⁻⁵. The growing interest in their physicochemical properties has been mostly stimulated by the recent developments in material sciences and nanotechnology^{6,7}. The vast amount of experimental information is complemented by quantum chemical calculations and by an

analysis of their electronic structure, which not only leads to a better interpretation of the experimental results but also provides fundamental insight into the molecular properties of these compounds⁸⁻¹¹.

Our theoretical endeavours to understand the details of the electronic structure of the octahedral Ru(II/III) and Os(II/III) complexes were initiated by theoretical calculations of the reduction potentials of a series of [Ru(bipy)₂X]^{2+/3+} complexes (where X stands for ethynyl-, 4-boronophenyl-, [(9-benzyladenin-8-yl)ethynyl]- and [4-(9-benzyl-adenin-8-yl)phenyl]-bipyridines or phenanthrolines)¹². Reasonable agreement between experiment and theory (a standard deviation of 0.13 V) allowed us to conclude that the theoretical calculations may possess some predictive power for the Ru(II) complexes and may assist in the search for new types of complexes with the desired values of their reduction potentials (e.g. candidates for electrochemical DNA labelling)¹³.

Moreover, it has been shown that the significantly poorer agreement between the calculated values of the reduction potentials for the [OsL₆]^{2+/3+} complexes obtained using standard density functional methods (with the effective core potentials to account for the scalar relativistic effects) is caused by the neglect of the spin-orbit coupling (SOC), which accounts for the systematic shifts in the reduction potentials of approximately -70 mV for the ruthenium(II/III) complexes and approximately -300 mV for the osmium(II/III) complexes¹⁴. More precisely, the SOC splits the three near-degenerate Kramers' doublets (which in an ideal octahedral symmetry corresponds to the zero-field splitting of the ²T_{2g} ground state) in the Os³⁺ (Ru³⁺) oxidation state and thus provides the extra stabilisation of the oxidised form when compared to the reduced form, which gives rise to a negative shift of the reduction potential. The equilibrium geometries of some representatives of the studied complexes are depicted in Fig. 1.

In this study, we present several interesting findings related to the electronic and geometrical structure of the octahedral Ru^{2+/3+} and Os^{2+/3+} complexes. First, the excitation spectra calculated using the TD-DFT and MRCI methods for the six model complexes and various spin multiplicities are presented, and their dependence on the ligand-field strength is discussed. The model complexes include the most prototypical Ru(Os)^{2+/3+} systems (i) hexahydrates of Ru^{2+/3+} and Os^{2+/3+}, (ii) [M(NH₃)₆]^{2+/3+} and [M(en)₃]^{2+/3+}, (iii) [MCl₆]^{4-/3-}, (iv) [M(CN)₆]^{4-/3-} and (v) [M(bipy)₃]^{2+/3+} (in all these cases M = Os, Ru). Second, we demonstrate the effect of the molecular geometry on the energy differences between the different spin states and on the multiplicity of the ground electronic state. This effect is most profound for neg-

actively charged and weak ligand-field complexes, such as the $[\text{MX}_6]^{4-/3-}$ systems ($\text{X} = \text{F}, \text{Cl}, \text{Br}$), and is analysed on the example of $[\text{MCl}_6]^{4-/3-}$. We show that the inclusion of the solvent effect into the calculations via the polarised continuum model (PCM) scheme changes the multiplicity of the ground electronic state. It is an interesting example of the solvatochromism and solvatomagnetism, i.e. the effect of a solvent on the electronic and magnetic properties of molecular systems¹⁵⁻¹⁷.

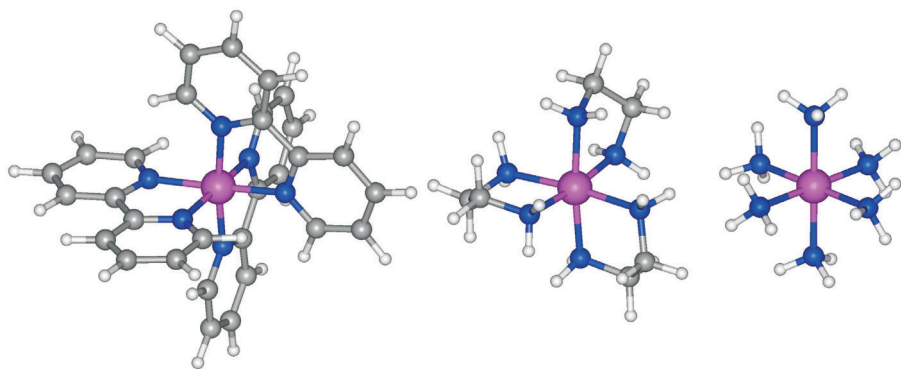


FIG. 1

The equilibrium structures of three representatives of the octahedral Ru(II/III) and Os(II/III) complexes: $[\text{M}(\text{bipy})_3]^{2+/3+}$, $[\text{M}(\text{en})_3]^{2+/3+}$ and $[\text{M}(\text{NH}_3)_6]^{2+/3+}$. The geometry optimisation was carried out at the DFT(PBE)/def2-SVP (including effective core potentials (ECPs) for Ru and Os) level. The metal–ligand distances are approximately 2.06, 2.14 and 2.13 Å for $\text{Ru}^{2+}\text{-N}_{\text{bipy}}$, $\text{Ru}^{2+}\text{-N}_{\text{en}}$ and $\text{Ru}^{2+}\text{-N}_{\text{NH}_3}$ (2.08, 2.16 and 2.15 Å for $\text{Os}^{2+}\text{-N}_{\text{bipy}}$, $\text{Os}^{2+}\text{-N}_{\text{en}}$ and $\text{Os}^{2+}\text{-N}_{\text{NH}_3}$) and 2.07, 2.12 and 2.11 Å for $\text{Ru}^{3+}\text{-N}_{\text{bipy}}$, $\text{Ru}^{3+}\text{-N}_{\text{en}}$ and $\text{Ru}^{3+}\text{-N}_{\text{NH}_3}$ (2.09, 2.15 and 2.14 Å for $\text{Os}^{3+}\text{-N}_{\text{bipy}}$, $\text{Os}^{3+}\text{-N}_{\text{en}}$ and $\text{Os}^{3+}\text{-N}_{\text{NH}_3}$) (cf. ref.¹⁴)

COMPUTATIONAL METHODS

DFT/ECP Calculations

All the density functional theory (DFT) calculations reported in the study were carried out using the Turbomole 5.8 program¹⁸. The Perdew–Burke–Ernzerhof (PBE)¹⁹ and Becke’s three-parameter hybrid (B3LYP)²⁰ functionals were used throughout. The calculations using a generalised gradient approximation (i.e. a non-hybrid functional, in our case PBE) were further expedited by expanding the Coulomb integrals in an auxiliary basis set, by a so-called resolution-of-identity (RI-J) approximation^{21,22}. All the geometry optimisations were carried out using the def2-SVP basis set²³, whereas the

single-point energies were recomputed in a larger basis set, def2-TZVP (triple-zeta valence with two polarisation functions on each atom)²³.

To enable the solvation effects, the conductor-like screening model (COSMO) method^{24,25} was used with the dielectric constant corresponding to water ($\epsilon_r = 80$) as implemented in Turbomole 5.8.

TD-DFT Calculations

In order to interpret and predict the spectra of the studied molecules, the TD-DFT method²⁶⁻²⁹ employing the Turbomole program³⁰ was used in conjunction with the PBE and B3LYP functionals and def2-TZVP basis set.

MRCI Calculations

The multireference configuration interaction (MRCI) calculations with an *a posteriori* selection of configurations³¹⁻³⁴, and the CASSCF calculations used for generating input molecular orbitals for the subsequent MRCI were carried out using the ORCA 2.6.35 program³⁵. The TZV-DKH basis set was used, which is based on Ahlrichs' TZVP basis set (contracted to [17s11p8d3f] for Os, [12s10p5d] for Ru and [8s4p1d] for Cl)³⁶, and contracted Neese's for relativistic calculations³⁵. Spin-free relativistic effects were included in all the calculations through the DKH2 Hamiltonian.

The MRCI calculations were performed in several steps using the DFT/ECP equilibrium geometries: (i) the state-specific CASSCF (6 electrons in 5 orbitals) calculations for the singlet ground state of the Ru²⁺/Os²⁺ complexes and the state-averaged CASSCF (5-in-5) calculations for the three lowest doublets of the Ru³⁺/Os³⁺ complexes, carried out to generate the input molecular orbitals for the MRCI; (ii) MRCI calculations of the energy stabilisation of the singlet and doublet ground states of the Ru²⁺/Os²⁺ and Ru³⁺/Os³⁺ complexes, respectively, due to the SOC with higher states of the appropriate spin multiplicities (up to quintets for Ru²⁺/Os²⁺ and sextets for Ru³⁺/Os³⁺), performed by means of the first-order QDPT using the mean-field spin-orbit Hamiltonian³⁷ as perturbation. The second-order Douglas-Kroll-Hess (DKH2) one-electron spinless Hamiltonian was applied to all the calculations to account for spin-free (one-component) relativistic effects³⁸⁻⁴⁰.

Threshold values for the configuration selection of 10⁻⁵ a.u. for the reference space ((6-in-5) for the M²⁺ and (5-in-5) for the M³⁺ complexes) and of 10⁻⁵ a.u. for the CI-SD space were used, which should presumably be a good approximation to the so-called second-order CI (MRCI-SD with a CAS

reference space without an *a posteriori* selection of configuration). An orbital window from -3 to 3 a.u. for the Ru complexes and from -1.9 to 2 a.u. for the Os complexes was used in the MRCI calculations.

RESULTS AND DISCUSSION

Excitation Energies in the Octahedral Ru(II/III) and Os(II/III) Complexes. TD-DFT Calculations

A series of TD-DFT calculations has been carried out to obtain the excitation energies in all of the studied complexes ($[\text{M}(\text{H}_2\text{O})_6]^{2+/3+}$, $[\text{M}(\text{NH}_3)_6]^{2+/3+}$, $[\text{M}(\text{en})_3]^{2+/3+}$, $[\text{MCl}_6]^{4-/3-}$, $[\text{M}(\text{CN})_6]^{4-/3-}$ and $[\text{M}(\text{bipy})_3]^{2+/3+}$, $\text{M} = \text{Os}, \text{Ru}$). The results of the TD-DFT calculations are summarised in Tables I and II. In general, the TD-DFT method is considered as a fairly cheap and in some cases a reasonably accurate method for the calculations of excitation spectra. Its drawbacks are well known and include systems and excitations with a multireference character. Additionally, the method poorly describes double (and higher) excitations from the ground-state wave function. Nevertheless, it still often captures the trends and main characteristics of the spectrum. This can be demonstrated by good agreement of the calculated value of the most intensive MLCT peak in the $[\text{Ru}(\text{bipy})_3]^{2+}$ complex (S_7 and S_8 excitations in Table II) of 434 nm (23000 cm^{-1}) with the experimental value in an aqueous solution (452 nm, corresponding to 22120 cm^{-1})⁴¹. Furthermore, it can be seen that the density of the excited states and excitation energies strongly depend on the nature of the ligand. The smallest excitation energies, including singlet–triplet (S–T), singlet–quintet (S–5), doublet–quartet (D–Q) and doublet–sextet (D–6) gaps are found for the lowest-field ligand (Cl^-), i.e. for the $[\text{RuCl}_6]^{4-/3-}$ and $[\text{OsCl}_6]^{4-/3-}$ complexes. In $[\text{RuCl}_6]^{4-}$ attaining the *in vacuo* equilibrium geometry, the DFT calculations even predict the high-spin state (quintet) to be the ground state. This is a consequence of both the weak ligand field exercised by Cl^- ligands and the larger metal–ligand distances caused by the high negative charge of these complexes. The splitting of t_{2g} and e_g^* metal d-orbitals is then small enough to allow Hund's rule to prevail (and bring the electronic structures closer to the isolated ion, namely a high-spin quintet). Only after considering the equilibrium geometry in solvent (which leads to the shortening of the Ru–Cl bonds by ~ 0.2 Å due to the screening of the highly negative total charge of the system), is the low-spin state correctly predicted to be the ground state. The series continues with complexes containing oxygen as the donor atom (hexaaqua complexes), bipyridyl complexes (because of

TABLE I

The energy gaps between the ground state and the lowest states of the higher spin multiplicities for the $\text{Ru}^{2+}/\text{Os}^{2+}$ (triplets – T, quintets – 5) and $\text{Ru}^{3+}/\text{Os}^{3+}$ (quartets – Q, sextets – 6) complexes, calculated at the DFT(PBE,B3LYP)/def2-TZVP level of theory. All values are in cm^{-1}

System	S-T PBE	S-5 PBE	S-T B3LYP	S-5 B3LYP	System	D-Q PBE	D-6 PBE	D-Q B3LYP	D-6 B3LYP
$[\text{Ru}(\text{bipy})_3]^{2+}$	16892	38950	18091	42965	$[\text{Ru}(\text{bipy})_3]^{3+}$	23792	47039	25489	50974
$[\text{RuCl}_6]^{4-}$	1838	-104	1839	-870	$[\text{RuCl}_6]^{3-}$	6633	10825	6387	9803
$[\text{RuCl}_6]^{4-}$ solv. geom.	6944	10420	6964	9740	$[\text{RuCl}_6]^{3-}$	8827	14742	8647	13803
$[\text{Ru}(\text{en})_3]^{2+}$	22426	41786	21753	39601	$[\text{Ru}(\text{en})_3]^{3+}$	23575	43570	22345	40471
$[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$	12664	20062	12560	19116	$[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$	13620	23547	13534	22280
$[\text{Ru}(\text{NH}_3)_6]^{2+}$	21233	38779	20676	36911	$[\text{Ru}(\text{NH}_3)_6]^{3+}$	21812	40336	20647	37364
$[\text{Ru}(\text{CN})_6]^{4-}$	28811	64996	31904	67375	$[\text{Ru}(\text{CN})_6]^{3-}$	37789	72560	36436	69311
$[\text{Os}(\text{bipy})_3]^{2+}$	14559	35299	15479	37515	$[\text{Os}(\text{bipy})_3]^{3+}$	21762	44719	25156	49313
$[\text{OsCl}_6]^{4-}$	3530	3063	3777	3057	$[\text{OsCl}_6]^{3-}$	8528	14174	8579	13882
$[\text{Os}(\text{en})_3]^{2+}$	25831	50499	26420	49666	$[\text{Os}(\text{en})_3]^{3+}$	27896	51366	27418	49620
$[\text{Os}(\text{H}_2\text{O})_6]^{2+}$	16594	27981	16765	27807	$[\text{Os}(\text{H}_2\text{O})_6]^{3+}$	16982	31074	17286	30878
$[\text{Os}(\text{NH}_3)_6]^{2+}$	24409	47443	25459	46960	$[\text{Os}(\text{NH}_3)_6]^{3+}$	25860	47858	25229	46249
$[\text{Os}(\text{CN})_6]^{4-}$	35035	75084	36460	80435	$[\text{Os}(\text{CN})_6]^{3-}$	41219	83257	45265	82351

TABLE II

The energies of the lowest excited states of the different spin multiplicities for the $\text{Ru}^{2+}/\text{Os}^{2+}$ (singlets, triplets) and $\text{Ru}^{3+}/\text{Os}^{3+}$ (doublets, quartets) complexes, calculated at the DFT(B3LYP)/def2-TZVP level of theory. All values are in cm^{-1} , the lowest state of a given spin multiplicity has been assigned a value of 0 cm^{-1}

System	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈	S ₉	S ₁₀
$[\text{Ru}(\text{bipy})_3]^{2+}$	20089	20218	20222	21671	21824	21836	23041	23047	24793	26420
$[\text{RuCl}_6]^{4-}$	8101	8135	8158	13174	13238	13264	34845	34854	34869	35182
$[\text{Ru}(\text{en})_3]^{2+}$	27193	27446	28037	31912	32140	32424	33238	33336	33467	35833
$[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$	19061	19095	19115	24491	24497	25328	35986	36134	36144	44870
$[\text{Ru}(\text{NH}_3)_6]^{2+}$	26307	26319	26488	29429	29664	29736	31492	31546	31721	38531
$[\text{Ru}(\text{CN})_6]^{4-}$	35082	35090	35091	35111	35125	35134	35155	35200	35223	35888
$[\text{Os}(\text{bipy})_3]^{2+}$	17435	18217	18227	19823	19840	20157	21761	21763	23389	24173
$[\text{OsCl}_6]^{4-}$	9492	9538	9556	14056	14133	14182	30846	30892	30946	40243
$[\text{Os}(\text{en})_3]^{2+}$	27700	29553	29753	30978	31349	32175	32911	33824	34115	34671
$[\text{Os}(\text{H}_2\text{O})_6]^{2+}$	22655	22658	22679	26724	26734	28425	30128	30993	31000	40309
$[\text{Os}(\text{NH}_3)_6]^{2+}$	25119	25584	25724	30110	30159	30417	34172	34328	34679	35181
$[\text{Os}(\text{CN})_6]^{4-}$	38177	38182	38188	41771	41787	42205	42222	42228	42257	44236

TABLE II
(Continued)

System	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈	D ₉	D ₁₀	D ₁₁
[Ru(bipy) ₃] ³⁺	2784	2808	14268	14277	14534	23392	23396	23426	24162	24175
[RuCl ₆] ³⁻	1352	1415	9515	10221	10459	11380	14258	15576	15850	18662
[Ru(en) ₃] ³⁺	2299	2465	25567	26198	26301	27246	27844	27983	28849	30290
[Ru(H ₂ O) ₆] ³⁺	4348	6279	17023	17542	17793	19928	22722	23156	23188	26802
[Ru(NH ₃) ₆] ³⁺	1583	1699	24034	24710	24826	25701	28953	30571	30919	34321
[Ru(CN) ₆] ³⁻	930	966	19833	20428	20509	23292	23437	23526	25403	25458
[Os(bipy) ₃] ³⁺	3000	3009	16206	16219	16429	23284	23299	23359	25040	25283
[OsCl ₆] ³⁻	1073	1131	11727	12294	12428	13177	15915	17084	17526	20067
[Os(en) ₃] ³⁺	2457	2696	30213	30723	30839	31668	31825	31968	32736	34371
[Os(H ₂ O) ₆] ³⁺	5032	7305	20758	21923	22179	24039	25971	26106	26844	29121
[Os(NH ₃) ₆] ³⁺	1696	1815	28549	29131	29212	29976	32865	34374	34641	37864
[Os(CN) ₆] ³⁻	863	895	21484	22015	22032	24155	24311	24331	26253	26265
	T ₂	T ₃	T ₄	T ₅	T ₆	T ₇				
[Ru(NH ₃) ₆] ²⁺	3095	3372	3711	8689	17839	17871				
	Q ₂	Q ₃	Q ₄	Q ₅	Q ₆	Q ₇				
[Ru(NH ₃) ₆] ³⁺	2551	2970	3177	18123	28675	28941				
[Os(NH ₃) ₆] ³⁺	2726	3096	3153	25880	28748	30875				

low-lying, empty ligand π^* orbitals) and sp^3 -nitrogen containing species (NH_3 , en); by far the highest excitation energies are found for the $[\text{Os}(\text{CN})_6]^{4-/3-}$ system. When comparing Os and Ru ions, it is worth mentioning that the excitation energies are in general slightly higher for the former (with the exception of the bipyridyl complexes).

*Excitation Energies in the $[\text{MCl}_6]^{4-/3-}$ Complexes ($M = \text{Ru}, \text{Os}$).
MRCI Calculations*

The MRCI calculations were carried out with the aim of further investigating the above phenomenon that was observed for the hexachloro ruthenium(II) complex, i.e. the existence of a low-lying quintet state, which becomes the ground state of the *in vacuo* (gas-phase) structure of this highly charged system. Figure 2 depicts the dependence of the energy of the three electronic states of various spin multiplicities (each of them being the lowest in the given spin multiplicity) on the molecular geometry (M–L distance). How their relative order changes when passing from the gas phase to the structure stabilised in the implicit-water environment is also demonstrated. The SOC effect on these three states is considered within a window of 15 singlet, 10 triplet and 5 quintet states (for $\text{Ru}^{2+}/\text{Os}^{2+}$), or of 15 doublet, 10 quartet and single sextet states (for $\text{Ru}^{3+}/\text{Os}^{3+}$). All the intermediate structures were obtained by an interpolation of the molecular geometries between the *in vacuo* and solvent structures.

Owing to the spin crossover, the $[\text{RuCl}_6]^{4-}$ species seems to be the most attractive. While this complex is predicted to be diamagnetic (a closed-shell d^6 system) in a water-like environment (near $\epsilon_r = 80$) which is in agreement with the general observation for the d^6 octahedral transition metal complexes in the 4d and 5d series⁴², the species can become hypothetically paramagnetic (an open-shell system with four unpaired d electrons) with the decreasing dielectric constant of a solvent. Hence, there is an exciting possibility to tune the magnetic properties and electronic spectrum via solvent effects (the latter are called the solvatochromic and solvatomagnetic effects). Some arguments explaining this electronic (and potentially magnetic) dependence were given in the previous section. Regarding the *in vacuo* equilibrium structure, it can be noticed that the three quintet states (which split into 15 sublevels due to the SOC in the C_1 symmetry) actually lie below the lowest singlet state. Besides the above mentioned effect of weak crystal field of the chloride ligands that causes the spin crossover, the existence of these fifteen states in the range of 1000–1100 cm^{-1} can also suggest the strong vibronic couplings between two (or more) of them,

which would lead to a further stabilisation of the lowest quintet state (i.e. to the pseudo Jahn–Teller effect). It is apparent for the $[\text{RuCl}_6]^{4-}$ complex that even though the SOC effect on the absolute energies of the lowest states is generally small, its manifestation is most pronounced in the *in vacuo* geometry ($\epsilon_r = 1$ in Fig. 2). The triplet state (which splits into three sublevels due to the SOC) becomes more stable than the lowest singlet

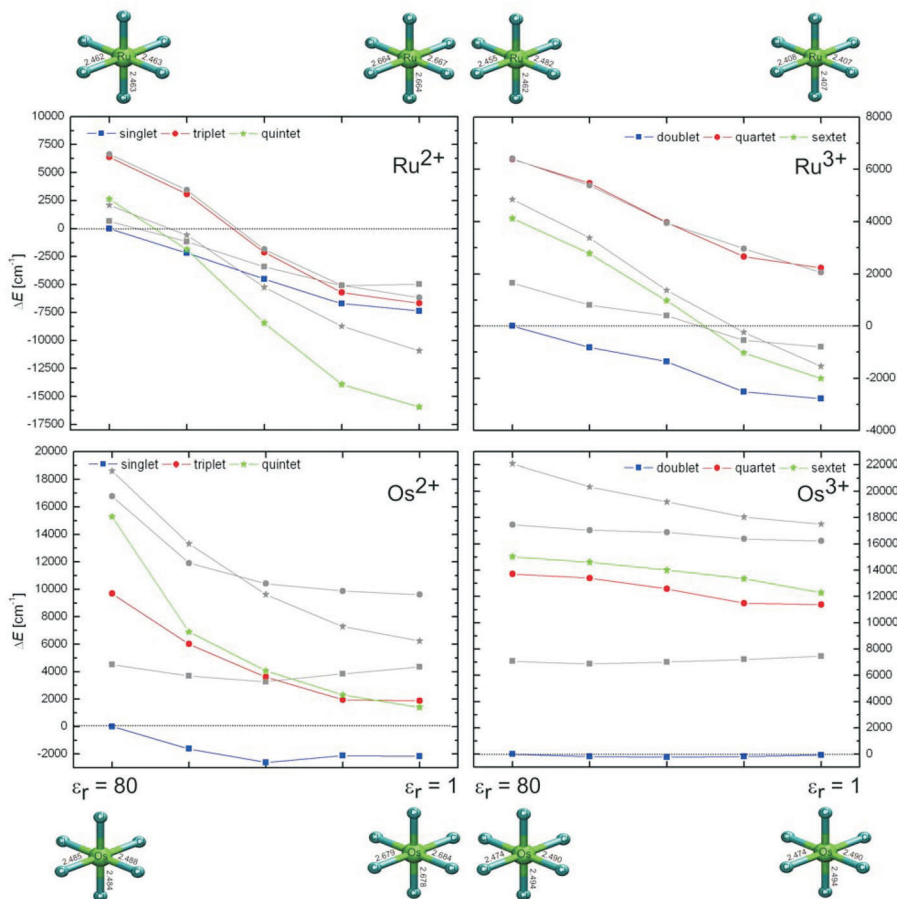


FIG. 2

The energies of the lowest electronic states of each multiplicity with respect to the change in the geometry (M–L distances) of the $[\text{RuCl}_6]^{4-/3-}$ and $[\text{OsCl}_6]^{4-/3-}$ complexes. Two extreme equilibrium structures (obtained from the *in vacuo* and implicit solvent optimisations) with their bond distances (in Å) are depicted for each of the studied complexes. The coloured and grey curves correspond to the SOC-corrected and spin-free relativistic energies, respectively

state. The ordering of the studied electronic states is less complicated in the $[\text{OsCl}_6]^{4-}$ complex, which remains diamagnetic in the range of the studied geometrical changes. The monotonous contraction of the singlet–triplet and singlet–quintet gaps when passing from the ‘*solvated*’ to the ‘*in vacuo*’ geometries can be attributed to the weakening ligand field and the diminishing gap between the t_{2g} and e_g^* orbitals.

Both paramagnetic $[\text{RuCl}_6]^{3-}$ and $[\text{OsCl}_6]^{3-}$ species have been stabilised in a doublet state for all the geometries. In an ideal octahedral symmetry, the SOC splits the six times (three times in the spatial and twice in the spin component) degenerate ${}^2T_{2g}$ state into three Kramers’ doublets. This is reflected by the near-degeneracy of the three lowest-lying Kramers’ doublets in the real, symmetry-perturbed (C_1) complexes. As a consequence, a stabilisation of the ground state by the SOC is more profound than in the $\text{Ru}^{2+}/\text{Os}^{2+}$ analogues. Although the three doublets remain the lowest-lying states in all the $[\text{OsCl}_6]^{3-}$ geometries studied, this is not true for $[\text{RuCl}_6]^{3-}$. In the *in vacuo* limit, three out of six sublevels of the zero-field split sextet lie between the doublet ground state and the first two excited doublets.

However, when discussing the small energy differences between the states of various multiplicities, one has to be aware of two limitations inherent in the calculations. First, a fair judgment would be that neither MRCI nor DFT can yield results of sufficient accuracy to assign the nature of the ground state clearly if the energy differences between the states with different multiplicities are below 0.1 eV (800 cm^{-1}), i.e. when they are comparable with the error bar of the methods⁴³. Second, it has been shown that for the smaller $\text{Ru}^{2+/3+}$ and $\text{Os}^{2+/3+}$ complexes, the PCM-like models can suffer from certain limitations, usually manifested in the incorrect description of the system’s energetics^{14,44}. As a consequence, these models do not yield sufficiently accurate values of the reduction potentials or other quantities which depend on the accuracy of the calculated values of solvation energies (e.g. the reduction potential of the $[\text{Ru}(\text{H}_2\text{O})_6]^{2+/3+}$ system)⁴⁴. As a possible solution to this deficiency, it has been proved that the addition of several explicit solvent molecules (a second solvation shell) generally improves the calculated values of the solvation energies^{14,44}. Nevertheless, for the purposes of this work (i.e. establishing the effect of solvent on molecular geometry), we consider the PCM models as a sufficiently accurate approximation.

CONCLUSIONS

In this study, we have presented the results of TD-DFT and MRCI (including spin-orbit coupling) calculations for the prototypical octahedral ruthenium(II/III) and osmium(II/III) complexes. First, we have shown that the TD-DFT excitation energies correlate well with the empirical ligand-field strength of the studied ligands (and with the experimental data when available). In the case of the hexachloro ruthenium(II) complex, this surprisingly led to an inversion of the spin multiplicity of its ground state in the *in vacuo* equilibrium geometry, and that in both the DFT and MRCI/QDPT calculations. The inclusion of the solvent effect into the calculations via the polarised continuum model (PCM) scheme then changes the equilibrium geometry of this complex and reverses the multiplicity of the ground electronic state with a closed shell singlet being correctly predicted as the ground state.

However, our findings suggest the tempting possibility of changing the electronic and magnetic properties of some of the $[\text{MX}_6]^{4-}$ systems ($X = \text{F}, \text{Cl}, \text{Br}$) via the solvatochromic or solvatomagnetic effects (changing the dielectric constant of the solvent). Also, it did not escape our notice that the $[\text{RuCl}_6]^{4-}$ complex in its lowest triplet and quintet states is unstable and spontaneously dissociates in the *in vacuo* geometry optimization. It invokes the idea of the existence of photochemically interesting system – exciplex. This property of hexachloro ruthenium(II) complex will be further investigated.

Last but not least, two important phenomena that have not been discussed here but have been noticed in the equilibrium structures of the studied complexes are the Jahn–Teller and pseudo-Jahn–Teller effects, which distort the molecular geometries of some of these octahedral complexes. However, this issue will be addressed elsewhere.

Supporting Information Available

The equilibrium geometries of all the studied molecules are available free of charge via doi:10.1135/cccc20081231.

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