Is the Ground State of $[RuO_4]^{2-}$ Exceptional?†

Robert J. Deeth
Inorganic Computational Chemistry Group, School of Chemistry, University of Bath, Bath BA2 7AY, UK

Optimised geometries of $[RuO_4]^{n-}$ (n = 0, 1 or 2) have been obtained. While the local density approximation (LDA) of density functional theory (DFT) gives good Ru–O distances for RuO_4 and $[RuO_4]^-$, the computed bond length for $[RuO_4]^{2-}$ is at least 0.07 Å too long. The latter result assumes a conventional $^3A_1$ electronic structure with the two notional d electrons in the essentially antibonding e molecular orbitals. However, a ^3E state, derived from the $e^1a_1^1$ configuration, is very close in energy and gives a far more satisfactory Ru–O distance although theory does not categorically establish ^3E as the outright ground state even after the inclusion of spin-polarisation, lattice, relativistic, Jahn–Teller and non-local functional effects. If the real ground state is ^3E then the DFT state energies for $[RuO_4]^{2-}$ would appear to be in error by about 10 kcal mol^{-1}. It seems more plausible to accept this error in total energy than the large bond length error associated with the $^3A_1$ state and therefore to conclude that the ground state for tetrahedral $[RuO_4]^{2-}$ is ^3E.

Ruthenium exhibits an extensive high oxidation state, oxo chemistry spanning Ru^{IV} through to Ru^{VIII}.[1] Many ruthenium complexes are catalytic oxidants either in their own right or in conjunction with other species like $[BrO_3]^-$.[2] The simplest ruthenium–oxo species are the tetraoxo complexes RuO_4, $[RuO_4]^-$ and $[RuO_4]^{2-}$ although the latter has been the subject of some confusion in that, in aqueous solution at high pH, the species formulated as $[RuO_4]^{2-}$ is actually the trigonal-bipyramidal $[RuO_3(OH)_2]^{2-}$ ion.[2] However, the recent high-temperature synthesis and crystal structure analysis of Cs_2RuO_4 has completed the structural characterisation of the tetrahedral complexes.[3–5]

As part of a series of density functional theory (DFT) studies of transition-metal species containing terminal M=O bonds,[6] calculations of the geometric and electronic structures of these ruthenium complexes have been undertaken. Among the previous studies are DFT treatments of the geometries[6a] and vibrational energies[6b] of the first-row, isovalent series $[CrO_4]^{2-}$, $[MnO_4]^{2-}$ and $[FeO_4]^{2-}$. In contrast to Hartree–Fock theory where the difference between observed and computed M=O distances increases on crossing the first transition series, the quantitative treatment of these systems by DFT is uniformly good.[6]

At a more qualitative level, the picture of the electronic structure of simple tetrahedral oxo complexes seems straightforward. The d^n electrons of the metal in its formal oxidation state are housed in the d-antibonding e and t_2 molecular orbitals (MOs). While the results reported below for d^0 RuO_4 and d^1 $[RuO_4]^-$ are as expected when compared to the DFT results on the isoelectronic first-row tetraoxo complexes of d^0 Cr^{VI} and d^1 Mn^{VI}, $[RuO_4]^{2-}$ did not behave like $[FeO_4]^{2-}$. On the basis of the DFT data, it is suggested that the accepted picture of the electronic structure of the apparently simple, formally d^2 $[RuO_4]^{2-}$ anion may need revising.

Computational Details

All DFT calculations were based on the Amsterdam density functional (ADF) program system due to Baerends *et al.*[7] The method employs Slater type orbital (STO) basis sets[8,9] and some applications have recently been reviewed by Ziegler.[10] The uniform electron gas local density approximation[11] (LDA) was used in conjunction with analytical energy gradients[12] for all geometry optimisations. The LDA correlation energy was computed according to Vosko, Wilk and Nusair's[13] parameterisation of electron gas data and includes Stoll's[14,15] correction for self-interaction. Non-local generalised gradient approximation (GGA) calculations of geometries and total binding energies employed the exchange and correlation correction terms of Becke[16] and Perdew[17,18] respectively. The lower core shells on the atoms (1s on O and up to 3d on Ru) were treated by the frozen-core approximation.[19] The total molecular electron density was fitted in each SCF cycle by auxiliary s, p, d, f and g STO functions.[20]

The basis sets are labelled according to whether they are double-ζ (DZ) or triple-ζ (TZ). In addition, the bases were augmented by including a 5p function on the metal and 3d polarisation functions on the oxygens which should ensure sufficient basis set flexibility. It has been shown[21] that DFT is less sensitive than Hartree–Fock theory to the inclusion of multiple polarisation functions and our experience suggests that no significant improvements arise from bases with additional diffuse functions to those described above, even for anionic oxo systems.

Results and Discussion

The good DFT results obtained previously for the first-row $[MO_4]^{2-}$ series of complexes, M = Cr, Mn and Fe, suggested that the valence isoelectronic $[RuO_4]^{n-}$ series should yield similarly accurate results. However, the first clues that some unusual features may be present in the Ru series are the reported Ru–O distances.[3–5] The expected electronic structure of a tetrahedral metal–oxo complex[1a] gives the valence configuration, $1t_1^6\,2e^n\,4t_2^0\,3a_1^0$ which places the antibonding e ($d_{x^2-y^2}$, d_{z^2}) orbitals above the t_1 oxygen based set as shown in Fig. 1. The e orbital population would therefore be expected to increase from zero to two across the series RuO_4 to $[RuO_4]^{2-}$ and one might have anticipated a monotonic variation in the Ru–O distance.

Sure enough, if one employs these orbital occupations in the DFT calculations, a monotonic increase in the Ru–O distances is found (Table 1). The LDA bond lengths increase from about 1.73 to 1.77 to 1.83 Å while the GGA values are systematically larger and increase from 1.76 to 1.80 to 1.86 Å. The GGA results, while excellent for $[RuO_4]^-$ are relatively poorer for RuO_4. The difference between DZ and TZ results is small.

---

† *Non-SI units employed:* cal ≈ 4.184 J, eV ≈ 1.602 × 10^{-19} J.

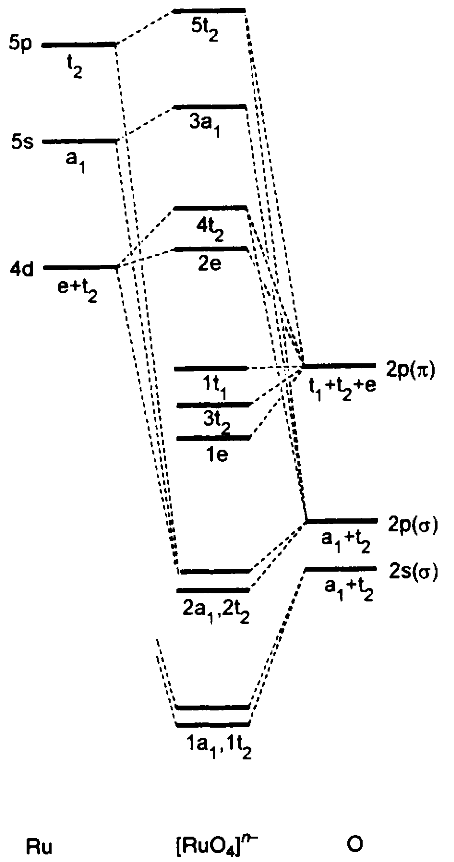

Fig. 1 Qualitative molecular orbital energy level diagram for $[RuO_4]^{n-}$ species

Table 1 Computed and observed Ru–O distances (Å) for progressive occupation of the valence 2e orbitals

Complex	Method	Basis	Ru–O
RuO_4	LDA	DZ	1.731
(e^0)	LDA	TZ	1.728
	GGA	DZ	1.754
	GGA	TZ	1.763
	Exptl.[a]		1.71
$[RuO_4]^-$	LDA	DZ	1.775
(e^1)	LDA	TZ	1.769
	GGA	DZ	1.800
	GGA	TZ	1.795
	Exptl.[b]		1.79
$[RuO_4]^{2-}$	LDA	DZ	1.831
(e^2)	LDA	TZ	1.824
	GGA	DZ	1.858
	GGA	TZ	1.851
	Exptl.[c]		1.763

[a] Ref 3. [b] Ref 4. [c] Ref 5.

These data were obtained using a closed-shell, spin-restricted (or spin-unpolarised) treatment. Given the presence of unpaired electrons in $[RuO_4]^-$ and $[RuO_4]^{2-}$, an open-shell, spin-polarised calculation, where the up-spin and down-spin electrons are treated independently, might be expected to yield better results for these anions. However, there were no significant changes in the optimised Ru–O distances for spin-polarised calculations. A similar result emerged for the first-row $[MO_4]^{2-}$ species[6] and for a range of d^9 chlorocuprate complexes.[22] Evidently, spin-restricted and spin-unrestricted DFT treatments of metal complexes with up to two unpaired electrons give very similar geometries.

On balance, the LDA results appear to be better in as much as the computed Ru–O distances for *both* RuO_4 and $[RuO_4]^-$ are within 0.02 Å of experiment. A comparable error has been found in other DFT treatments of RuO_4[23] and for species such as $[MO_4]^{2-}$ (M = Cr, Mn or Fe)[6a] and MO_2X_2 (M = Cr or Mo, X = F or Cl).[6c,23] It is not especially clear why the GGA results lead to apparently worse agreement, especially for RuO_4 which has been structurally characterised in the gas phase. GGA corrections for MO_2X_2 (M = Cr or Mo, X = Cl or F)[6c] give uniform bond lengthenings of 0.02–0.04 Å relative to the LDA results but in those cases, the GGA results were in better agreement with experiment. Here, the LDA optimised bond lengths already appear to be slightly too long and the GGA corrections serve to worsen this. Of course, gradient corrections were originally introduced to correct the relatively poor LDA *energies*.[10] While one might reasonably expect a better treatment of the energy to carry over into a better treatment of the geometry, this does not appear to be the case for the present ruthenium complexes. Further exploration of this problem is required.

Returning to the experimental Ru–O distances, we note that they apparently do not vary monotonically. Instead, they change from 1.705 Å in RuO_4[3] to 1.79 Å in $[RuO_4]^-$[4] to 1.763 Å in $[RuO_4]^{2-}$.[5] This conclusion depends on the experimental bond length uncertainties which for RuO_4 and $[RuO_4]^{2-}$ are less than 0.005 Å. An exact uncertainty was not given for $[RuO_4]^-$ although the error in the fractional coordinates was estimated to be 0.002. Unit cell parameters of a = 5.609 and c = 12.991 Å give a very crude estimate for the error in cartesian coordinates of around 0.016 Å which presumably implies an uncertainty in the Ru–O distance of around 0.03 Å. This could imply that $[RuO_4]^-$ and $[RuO_4]^{2-}$ have the same metal–ligand distance to within experimental error.

However, the more important point to emerge from the data in Table 1 is that the DFT computed Ru–O distance in $[RuO_4]^{2-}$ is significantly and anomalously too long given the small experimental uncertainty. Either DFT is failing in this case, which is difficult to accept given the reasonable treatment of the other two complexes, or there is a more subtle explanation. Assuming the latter, a series of fixed geometry calculations were performed using the observed Ru–O distance of 1.763 Å. Somewhat unusually, compared to the valence isoelectronic $[FeO_4]^{2-}$ ion,[6] it turns out that the (spin-restricted) e^2 ($^3A_1$) configuration leads to a non-Aufbau state with the vacant $3a_1$ MO now at a *lower* energy than the occupied 2e function.

This result is qualitatively different from the behaviour found for the first-row tetraoxo complexes which all obey the Aufbau principle. Of course, and as pointed out by a referee, there is no *a priori* reason why the ground state should also conform to the Aufbau principle. However, experience to date with other oxo complexes suggests that this is normally the case and the difference in behaviour therefore prompted a more detailed investigation as to the actual ground state of $[RuO_4]^{2-}$. Given the position of the $3a_1$ MO in $[RuO_4]^{2-}$, two other likely configurations were explored corresponding to $2e^1 3a_1^1$ (^3E) and $2e^0 3a_1^2$ ($^1A_1$) occupations. (Note that the $2e^1 3a_1^1$ configuration also gives a ^1E state at higher energy which is not considered further.) The data in Table 2 demonstrate that the ^3E state is quite close to $^3A_1$ although, at this point, it is always slightly higher by about 0.5 or 1.8 kcal mol^{-1} for the GGA and LDA calculations respectively.

The 2e MO rapidly decreases in energy for the states $^3A_1$ to ^3E to $^1A_1$ while the $3a_1$ function drops more slowly. The two orbitals cross over between the ^3E to $^1A_1$ states such that the latter has a vacant 2e orbital some 3.5 eV lower than the filled $3a_1$ level. However, the $^1A_1$ state is clearly an excited state being over 50 kcal mol^{-1} higher than either of the spin-triplet levels.

The main contender for the alternative ground state of $[RuO_4]^{2-}$ is thus ^3E. This state is Jahn–Teller active so, presumably, the molecule can distort to remove the orbital

Table 2 Calculated MO (eV) and total binding (kcal mol^{-1}) energies for $[RuO_4]^{2-}$ (Ru–O distance fixed at 1.763 Å, TZ basis sets)

Configuration	State	E(2e)	E($3a_1$)	E_{total}(LDA)	ΔE*	E_{total}(GGA)	ΔE*
e^2a^0	$^3A_1$	7.553	6.940	−699.6	0	−625.5	0
e^1a^1	^3E	4.336	5.591	−697.8	+1.8	−625.0	0.5
e^0a^2	$^1A_1$	1.366	4.858	−645.1	+54.5	−574.2	+51.3

* Energy relative to $^3A_1$.

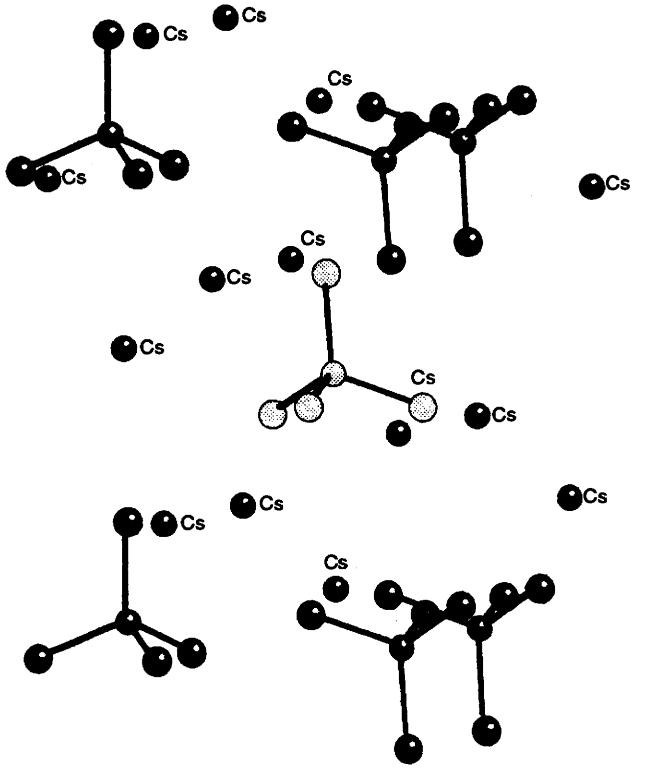

Fig. 2 Model used to simulate the lattice environment of a reference $[RuO_4]^{2-}$ anion (light spheres)

degeneracy and lower its energy. One would expect, therefore, to be able to compute the correct ground state by relaxing all spatial and spin restrictions. However, it turns out that the ^3E state leads to an essentially unwarped 'Mexican hat' potential energy surface[24] with a large number of more-or-less equi-energetic distorted geometries. Under these conditions, the calculation is unable to locate a stable minimum and oscillates. One is therefore obliged to maintain spatial (*i.e.* T_d or D_{2d}) symmetry.

Effect of the Crystalline Lattice.—Further attempts were made to investigate whether improving the calculation would establish ^3E as the outright ground state. To assess the possible influence of the crystal lattice, the $[RuO_4]^{2-}$ complex was imbedded in a field of point charges. In the Cs_2RuO_4 crystal, there are six other Ru atoms within a 6 Å radius of the central, reference Ru. To obtain an overall neutral cluster, the nearest 14 Cs^+ ions were located. These fell into three shells with six ions at about 4 Å, four ions at about 4.8 Å and the remaining four ions at about 7.4 Å from the central Ru. This yields an overall neutral cluster of formula $\{Cs_{14}[RuO_4]_7\}$ as shown in Fig. 2. The central $[RuO_4]^{2-}$ ion required slight idealisation to maintain T_d symmetry and facilitate identification of the relevant MOs but the resulting DFT calculation was run without symmetry constraint due to the low symmetry of the surrounding potential field. In all cases, a unit positive charge was used for the Cs ions but the Ru and O charges were self-consistently optimised such that the Mulliken charges arising from the DFT calculation of the reference $[RuO_4]^{2-}$ ion were within 0.01 of those used for the surrounding point charges. For the ^3E state, this gave Ru and O charges of 0.98 and −0.75 respectively while for $^3A_1$, the charges were 1.38 and −0.85 respectively.

The data in Table 3 show that the ^3E state is *destabilised* relative to the $^3A_1$ state by about 30 kcal mol^{-1} relative to the *in vacuo* data in Table 2.

Admittedly, these simulations of the crystalline environment are incomplete. The magnitudes of the charges in the actual crystal may be different since there may be some charge migration involving the Cs ions, and no account of the long-range Coulomb interactions is taken. Unfortunately, the available ADF version does not include facilities for Ewald summations and cannot therefore model the full crystal potential. Nevertheless, the most important nearest-neighbour interactions are included which should reflect the likely effect of the whole lattice semiquantitatively. One concludes that the lattice potential favours the $^3A_1$ state relative to ^3E by roughly 30 kcal mol^{-1}.

Relativistic Effects.—Non-relativistic DFT treatments of the geometries of second-row transition-metal systems are still capable of good accuracy.[6c,23,25] However, given the fine balance of the $^3A_1$ and ^3E energies and the possible geometry differences between the states (see above), the same may not hold for $[RuO_4]^{2-}$. Accordingly, the calculations summarised in Tables 2 and 3 were repeated with the relativistic correction described by Snijders *et al.*[26]

Relativity is incorporated into the ADF program using first-order perturbation theory where terms up to α^2, where α is the fine structure constant, are retained in the Hamiltonian. The results of these relativistically corrected calculations are given in Table 4.

The relativistic correction lowers ^3E relative to $^3A_1$ by up to about 6 kcal mol^{-1}. For the *in vacuo* GGA calculation, this actually results in an inversion of the state energies with the ^3E ($e^1a_1{}^1$) state lower than the $^3A_1$ ($e^2a_1{}^0$) state by about 3 kcal mol^{-1}. There are two remaining provisos, however. First, a spin-unrestricted *in vacuo* relativistic calculation restores $^3A_1$ to the ground state by about 3 kcal mol^{-1}. Secondly, the Ru–O distance has been kept fixed throughout and the resultant total binding energies do not correspond to total energy minima.

Total Binding Energies as a Function of a Bond Length.—Fig. 3 displays the *in vacuo* binding energies of $[RuO_4]^{2-}$ as a function of the Ru–O distance both with [(*a*) and (*b*)] and without [(*c*) and (*d*)] relativistic corrections. In no case is the ^3E state predicted to be the ground state although it is within about 10 kcal mol^{-1} of the $^3A_1$ level. However, a significant feature of Fig. 3 (and Table 5) is the optimum Ru–O distance. The computed non-relativistic LDA distance of 1.78 Å is now within the 0.02 Å tolerance of the experimental value of 1.763 Å paralleling the quality of result obtained for RuO_4 and $[RuO_4]^-$. The relativistic correction for all three molecules leads to a small contraction of about 0.01 Å giving for $[RuO_4]^{2-}$ virtually perfect agreement with experiment as shown in Table 5. These contractions are rather larger than found for $Mo(CO)_6$[27] although this molecule is very different to $[RuO_4]^{2-}$. Nevertheless, there seems to be a growing body of evidence that relativistic corrections for geometry optimisations

Table 3 Effect of lattice environment on computed MO (eV) and total (kcal mol^{-1}) energies for $[RuO_4]^{2-}$ (molecule idealised to T_d symmetry with Ru–O distances fixed at 1.763 Å, TZ basis sets)

Configuration	State	Lattice	E(2e)	E(3a$_1$)	E_{total}(LDA)	ΔE*	E_{total}(GGA)	ΔE*
e^2a^0	$^3A_1$	Point charge	−4.4	−3.3	−1257.4	0	−1185.1	0
e^1a^1	^3E	Point charge	−5.7	−4.0	−1229.2	+28.2	−1155.7	+29.4

* Energy relative to $^3A_1$.

Table 4 Effect of relativistic correction on computed MO (eV) and total (kcal mol^{-1}) energies for $[RuO_4]^{2-}$ (Ru–O distances fixed at 1.763 Å, TZ basis sets)

Configuration	State	Lattice	E(2e)	E(3a$_1$)	E_{total}(LDA)	ΔE*	E_{total}(GGA)	ΔE*
e^2a^0	$^3A_1$	None	7.700	6.992	−750.7	0	−675.1	0
e^1a^1	^3E	None	4.463	5.584	−751.7	+1.0	−678.2	−3.1
e^2a^0	$^3A_1$	Point charge	−4.2	−3.0	−1537.2	0	−1469.8	0
e^1a^1	^3E	Point charge	−5.4	−3.2	−1526.8	+10.4	−1460.5	+9.3

* Energy relative to $^3A_1$.

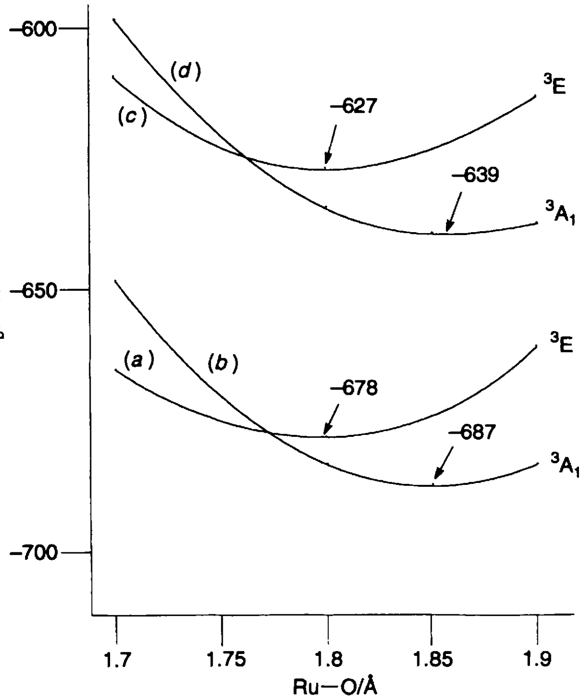

Fig. 3 Relative GGA binding energies, E_b (kcal mol^{-1}) for $[RuO_4]^{2-}$ as a function of Ru–O bond length (Å) with [(*a*) and (*b*)] and without [(*c*) and (*d*)] relativistic corrections. Energy minima indicated by arrows

Table 5 Optimised Ru–O distances (Å) for ^3E ($e^1a_1{}^1$) state of $[RuO_4]^{2-}$

Method*	Basis	Ru–O
LDA, non rel.	DZ	1.782
LDA, non rel.	TZ	1.781
GGA, non rel.	DZ	1.807
GGA, non rel.	TZ	1.804
LDA, rel.	TZ	1.766
GGA, rel.	TZ	1.794
Exptl.		1.763

* Non rel. = non relativistic, rel. = relativistic.

are still fairly small even for second-row metal complexes. Taking the non-relativistic Ru–O distances, therefore, one is now tempted to speculate that the computed $^3A_1$ state may not be the actual ground state of $[RuO_4]^{2-}$.

Table 6 Optimised geometries (Å and °) and relative energies (kcal mol^{-1}) of D_{2d} symmetry complexes (TZ basis sets)

Complex	Method	State	Ru–O	O–Ru–O^a	Relative energy^b
$[RuO_4]^-$	LDA	$^2A_1$	1.763	109.8	−6.1
	LDA	$^2B_1$	1.767	105.2	−8.6
	GGA	$^2A_1$	1.788	109.9	−6.4
	GGA	$^2B_1$	1.790	105.0	−8.6
$[RuO_4]^{2-}$	LDA	$^3A_1$	1.793	110.3	−5.6
	LDA	$^3B_1$	1.829	104.0	−10.2
	GGA	$^3A_1$	1.799	110.5	−5.9
	GGA	$^3B_1$	1.857	105.5	−6.2

^{a} Angle bisected by z axis. ^{b} GGA energy calculated relative to optimised T_d geometry under same computational conditions.

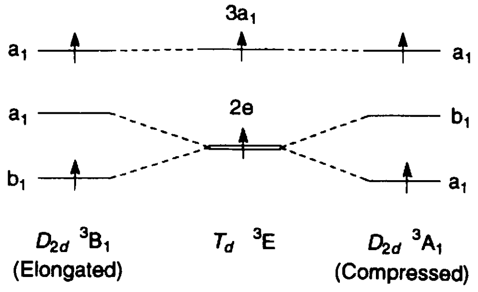

Fig. 4 Qualitative valence molecular orbital diagram for Jahn–Teller distortion of $[RuO_4]^{2-}$

Jahn–Teller Effects.—The ^2E and ^3E states of $[RuO_4]^-$ and $[RuO_4]^{2-}$ respectively are formally Jahn–Teller active although the effect should be relatively small given the weakly antibonding nature of the e orbitals in tetrahedral symmetry. Nevertheless, the resulting distortion does provide an additional mechanism for stabilising the ^3E state of $[RuO_4]^{2-}$ relative to the Jahn–Teller inactive $^3A_1$ level.

The optimised Ru–O distances and binding energies (relative to the relevant tetrahedral precursor) are given in Table 6. In the absence of a defined spatial symmetry (see above) the calculation does not converge and D_{2d} symmetry is assumed. This splits the original e orbital pair into an a_1 and a b_1 function generating two new electronic states of A_1 or B_1 symmetry. For $[RuO_4]^{2-}$, spin triplets have been maintained which leads the orbital occupations as shown in Fig. 4.

For both complexes, the energy stabilisation relative to the parent E state is of the order of 6 kcal mol^{-1} which is similar in magnitude to the relativistic correction. The A_1 states result in slightly compressed geometries while the B_1 states give elongated tetrahedra. The angular distortions are quite small, however, and the D_{2d} optimised bond lengths are virtually

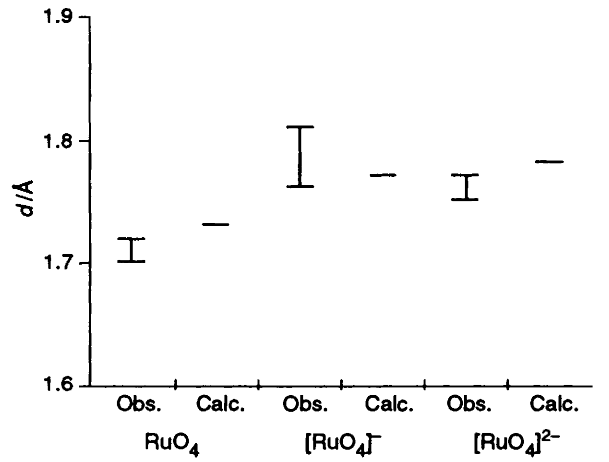

Fig. 5 Final best agreement between observed and calculated (closed-shell, LDA, non-relativistic) Ru–O bond lengths (Å). For the observed distances, approximate experimental error ranges are indicated. Calculated data for $[RuO_4]^{2-}$ assume a ^3E ground state

identical to their regular tetrahedral precursors. The magnitude of the energies and distortions involved is evidently not large enough for any static Jahn–Teller distortions to be observable. As discussed above, the minimum of the Mexican hat potential energy surface appears to be very flat.

Ruthenium–Oxygen Bond Lengths.—To summarise, the relativistic and Jahn–Teller corrections for $[RuO_4]^{2-}$ tend to stabilise ^3E relative to $^3A_1$ while spin-polarisation and lattice effects act in the opposite sense. Given the treatment of the lattice, one cannot be categoric but there does appear to be some mutual cancellation to the extent that phenomenologically, the *in vacuo*, non-relativistic LDA treatment gives reasonable agreement with experiment. This cancellation extends somewhat to the optimised bond lengths inasmuch as the increases accompanying the non-local GGA corrections are partially cancelled by the relativistic contractions. For both RuO_4 and $[RuO_4]^-$, the first excited states are well removed from the ground state and the various corrections described above have little effect. The most favourable comparison of observed (and calculated) bond lengths (in Å, see Fig. 5) is: RuO_4, 1.71 (1.73); $[RuO_4]^-$, 1.79 (1.77); $[RuO_4]^{2-}$, 1.76 (1.78) where a ^3E ground state is assumed for the latter. It appears that theory can reproduce experiment to within 0.02 Å for any given complex. However, as shown in Fig. 5, the variation across the series seems less impressive in that the observed Ru–O distances first change by +0.08 Å and then by −0.03 Å while the computed changes are +0.04 and +0.01 Å although such comparisons pivot on the Ru–O distance in $[RuO_4]^-$ which is relatively uncertain (see above). For the more accurately determined structures of RuO_4 and $[RuO_4]^{2-}$, DFT appears systematically to overestimate experiment. Given that the structure of the first molecule was determined in the gas phase where crystal-packing forces are absent, the fault appears to lie with DFT itself. However, a more accurate structure for the ruthenium(VII) complex would help clarify this issue.

The preceding also assumes a ^3E ground state for $[RuO_4]^{2-}$ and therefore that one is prepared to accept an error in the DFT binding energies of about 10 kcal mol^{-1}. Alternatively, one could accept a $^3A_1$ ground state in which case the optimised Ru–O distance in $[RuO_4]^{2-}$ is predicted to be at least 0.07 Å too long. Experience to date suggests that such large errors in geometrical features are less likely than a 10 kcal mol^{-1} uncertainty in a total binding energy. It is unclear why $[RuO_4]^{2-}$ appears to behave so differently from the other tetraoxometalates studied to date and further calculations are in hand on related ruthenium(VI) species like $[RuO_3(OH)_2]^{2-}$, *trans*-$[RuO_2Cl_4]^{2-}$ and the *cis* and *trans* forms of $[RuO_2Cl_3]^-$ to examine this feature. Assuming that the ^3E state is in fact the true ground state, it would also be of interest to investigate whether different non-local functionals can reverse the present result of a lower $^3A_1$ state.

Conclusion

The LDA DFT optimised geometries for RuO_4 and $[RuO_4]^-$ are in good agreement with experiment while comparable non-local GGA results are marginally worse. However, the predicted bond length for the expected $^3A_1$ (e^2) state of $[RuO_4]^{2-}$ is seriously overestimated. Detailed analysis indicates that the ^3E state derived from the $e^1a_1{}^1$ configuration is very close in energy. Extensive calculations of lattice, relativistic, spin-polarisation and Jahn–Teller effects suggest some mutual cancellation of errors. The relativistic and Jahn–Teller corrections favour a ^3E ground state while lattice effects and spin-polarisation favour $^3A_1$ and the expansion of the Ru–O distances when non-local GGA corrections are added is partially cancelled by a relativistic contraction. However, the calculations do not yield a ^3E ground state outright. Yet, the optimised Ru–O distance for ^3E is in much better agreement with experiment (within 0.02 Å) suggesting that if the DFT binding energies are in error by about 10 kcal mol^{-1}, which seems more reasonable than an error in the Ru–O distance of 0.07 Å, the actual ground state for nominally tetrahedral $[RuO_4]^{2-}$ should be ^3E and not $^3A_1$.

Acknowledgements

The author acknowledges the support of the Engineering and Physical Sciences Research Council and the Science and Materials Computing Committee for provision of computer hardware.

References

1 (*a*) W. P. Griffith, *Chem. Soc. Rev.*, 1992, **21**, 179; (*b*) R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401; (*c*) E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, New York, 1984.
2 A. J. Bailey, W. P. Griffith, S. I. Mostafa and P. A. Sherwood, *Inorg. Chem.*, 1993, **32**, 268 and refs. therein.
3 L. Schaefer and H. M. Seip, *Acta Chem. Scand.*, 1967, **21**, 737.
4 M. D. Silverman and H. A. Levy, *J. Am. Chem. Soc.*, 1954, **76**, 3317.
5 D. Fischer and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1990, **591**, 87.
6 (*a*) R. J. Deeth, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3745; (*b*) R. J. Deeth and P. D. Sheen, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 3237; (*c*) R. J. Deeth, *J. Phys. Chem.*, 1993, **97**, 11 625; (*d*) R. J. Deeth, *J. Chem. Soc., Dalton Trans.*, 1991, 1895; (*e*) R. J. Deeth, *J. Chem. Soc., Dalton Trans.*, 1991, 1467; (*f*) R. J. Deeth, *J. Chem. Soc., Dalton Trans.*, 1990, 365.
7 E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 41.
8 J. G. Snijders, P. Vernooijs and E. J. Baerends, *At. Data Nucl. Data Tables*, 1981, **26**, 483.
9 P. Vernooijs, G. P. Snijders and E. J. Baerends, *Slater Type Basis Functions for the Whole Periodic System*, Internal Report, Free University, Amsterdam, 1981.
10 T. Ziegler, *Chem. Rev.*, 1991, **91**, 651.
11 J. C. Slater, *Adv. Quant. Chem.*, 1972, **6**, 1.
12 L. Versluis and T. Ziegler, *J. Chem. Phys.*, 1988, **88**, 322.
13 S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200.
14 H. Stoll, E. Golka and H. Preuss, *Theor. Chim. Acta*, 1980, **55**, 29.
15 H. Stoll, C. M. E. Pavlidou and H. Preuss, *Theor. Chim. Acta*, 1978, **49**, 143.
16 A. J. Becke, *Chem. Phys.*, 1986, **84**, 4524.
17 J. P. Perdew, *Phys. Rev. B, Condens. Matter*, 1986, **33**, 8822.
18 J. P. Perdew, *Phys. Rev. B, Condens. Matter*, 1987, **34**, 7406 (erratum).
19 E. J. Baerends, D. E. Ellis and P. Ros, *Theor. Chim. Acta*, 1972, **27**, 339.

20 J. Krijn and E. J. Baerends, *Fit Functions for the HFS Method*, Internal Report, Free University, Amsterdam, 1984.
21 B. Delley and D. E. Ellis, *J. Chem. Phys.*, 1982, **76**, 1949.
22 R. J. Deeth and P. D. Sheen, unpublished work.
23 C. Sosa, J. Andzelm, B. C. Elkin, E. Wimmer, K. D. Dobbs and D. A. Dixon, *J. Phys. Chem.*, 1992, **96**, 6630.
24 R. J. Deeth and M. A. Hitchman, *Inorg. Chem.*, 1986, **25**, 1225.
25 R. J. Deeth, *J. Chem. Soc., Dalton Trans.*, 1993, 3711.
26 J. G. Snijders and E. J. Baerends, *Mol. Phys.*, 1978, **36**, 1789; J. G. Snijders, E. J. Baerends and P. Ros, *Mol. Phys.*, 1979, **38**, 1909.
27 J. Li, G. Schreckenbach and T. Ziegler, *J. Am. Chem. Soc.*, 1995, **117**, 486.

Received 2nd December 1994; *Paper* 4/07381I