J. Am. Chem. Soc. **2001,** *123,* 5495−5506

Protonation-Induced Paramagnetism. Structures and Stabilities of Six- and Seven-Coordinate Complexes of Os(II) in Singlet and Triplet States: A Density Functional Study

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Received October 19, 2000. Revised Manuscript Received March 28, 2001

Abstract: Li, Yeh, and Taube in 1993 (*J. Am. Chem. Soc.* **1993**, *115*, 10384) synthesized a number of complexes which can be formally regarded as protonated Os(II) species. Some of these were paramagnetic, in contrast to the diamagnetism of the closed shell $5d^6$ Os(II) ions. This intriguing phenomenon is investigated theoretically using density functional theory. The geometries, stabilities, and electronic structures of a series of six- and seven-coordinate osmium complexes were studied in gas phase and aqueous solution using the B3P86 functional, in conjunction with the isodensity-polarized continuum model of solvation. The general formula for these complexes is $[Os(NH_3)_4H(L_1{}^x)_m(L_2{}^y)_n]^{(x+y+3)+}$, where L_1 and $L_2 = H_2O$, NH_3, CH_3OH, CH_3CN, Cl^-, and CN^-, which could be regarded as protonated Os(II) species or hydrides of Os(IV), although according to this work the osmium−hydrogen interaction is best described as a covalent Os(III)−H bond, in which the hydrogen is near-neutral. The ground states are generally found to be singlets, with low-lying triplet excited states. Solvation tends to favor the singlet states by as much as $\sim$ 18 kcal mol^{-1} in the 3+ ions, an effect which is proportional to the corresponding difference in molecular volumes. To have realistic estimates of the importance of spin−orbit coupling in these systems, the spin−orbit energy corrections were computed for triplet $[Os(NH_3)_4]^{2+}$, $[Os(NH_3)_4H]^{3+}$, and $[Os(NH_3)_4H(H_2O)]^{3+}$, along with gas-phase Os and its ions as well as $[Os(H_2O)_6]^{3+}$. The seven-coordinate triplet-state complex $[Os(NH_3)_5H(CH_3OH)]^{3+}$, which had been successfully isolated by Li, Yeh, and Taube, is predicted to be a stable six-coordinate complex which strongly binds to a methanol molecule in the second coordination shell. The calculations further suggest that the singlet−triplet splitting would be very small, a few kilocalories per mole at most. The geometries and the electronic structures of the complexes are interpreted and rationalized in terms of Pauling's hybridization model in conjunction with conventional ligand field theory that effectively precludes the existence of true seven-coordinate triplet-state complexes of the above formula.

Introduction

In 1993, an interesting class of paramagnetic Os(IV) monohydrido complexes was synthesized and studied by Li, Yeh, and Taube.[1] The first two of these, prepared by the oxidation in methanol of (diamagnetic) $[Os(NH_3)_5(\eta^2\text{-}H_2)]^{2+}$ and $[Os(en)_2(\eta^2\text{-}H_2)]^{2+}$, were characterized as $[Os(NH_3)_5(H)(CH_3OH)]^{3+}$ and $[Os(en)_2(H)(CH_3OH)]^{3+}$ (en = ethylenediamine), i.e., seven- and six-coordinate species, respectively. As discussed by Li, Yeh, and Taube, the electronic structures of these complexes can be described as Os(IV)−H^- or as protonated Os(II) species. Li and Taube[2] also obtained a paramagnetic compound with the formula $[Os(NH_3)_4(H)(CH_3CN)_2](CF_3SO_3)_3$ by simply dissolving $[Os(NH_3)_4(CH_3CN)_2](CF_3SO_3)_2$ in 3 M triflic acid and successfully determined the equilibrium constant for the protonation reaction

$$[Os(NH_3)_4(CH_3CN)_2]^{2+} + H^+ \rightleftarrows [Os(NH_3)_4(H)(CH_3CN)_2]^{3+}$$

in water. Other possible seven-coordinate species include $[Os(NH_3)_5H(Fe(CN)_6)]^-$ and $[Os(en)_2H(py)_2]^{3+}$ (py = pyridine). In an earlier paper, Sullivan et al.[3] reported a NMR study of seven-coordinate Os(IV) complexes such as $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$ (bpy = 2,2′-bipyridine), also obtained by protonation of the six-coordinate parent compunds, viz. $[Os(bpy)(PPh_3)_2(CO)H]^{2+}$ in the case of the above example. On the basis of the NMR data, Sullivan et al.[3] proposed a pentagonal bipyramidal structure for $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$.

As the valence electronic configuration of the Os^{4+} ion is $5s^2 5p^6 5d^4$ (outside the $1s^2 ... 4f^{14}$ core), depending on the ligand field, the nonbonding d electrons in a Os(IV) complex could adopt high- or low-spin configurations, corresponding to quintet, triplet, or singlet states. In an (approximate) octahedral environment, the ligand field splitting between the t_{2g} nonbonding and e_g antibonding molecular orbitals (MO) in fourth- and fifth-row transition metal complexes is generally too large to allow for a $t_{2g}{}^3 e_g{}^1$-type configuration, but depending on the relative energies of the t_{2g} MOs, which in turn depend on the ligands and their arrangement around the metal, a $t_{2g}{}^4$ configuration could result in either a singlet or a triplet state.

A recent theoretical study of tungsten(I) carbonyl complexes by Büker et al.[4] provides a nice demonstration of the progression

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10.1021/ja003723r CCC: $20.00

from high to low spin with the increasing strength of the ligand field. Büker et al. found that for the series $W(CO)_n^+$ ($n = 1-6$), the electronic ground state is sextet for $n = 1$, quartet for $n = 2$, and doublet for $n = 3-6$.

The existence of the unusual molecules reported by Li et al.[1,2] has prompted us to undertake a theoretical study of a range of complexes of the type $[Os(NH_3)_4H(L_1^{x})_m(L_2^{y})_n]^{(mx+ny+3)+}$, where the ligands L_1 and L_2 are CH_3OH and NH_3 as well as H_2O, Cl^-, CN^-, and CH_3CN and m, $n = 0$, 1. Thus, for $m = n = 1$, we have formally seven-coordinate complexes, and it is primarily for these that the ground states are expected to be triplets. The main motivation for this study is to characterize the geometries of these molecules, to compare the structures and stabilities of each species in both triplet and (low-spin) singlet states, and to determine which, from the above group, may be expected to exist in addition to those observed by Li et al.,[1,2] and finally, how we can best understand and describe the electronic structures and properties of this interesting class of transition metal complexes. As part of our theoretical study, we have found it instructive to study also the six-coordinate complexes ($m = 1$, $n = 0$) as well as the hypothetical five- and four-coordinate parent systems $[Os(NH_3)_4H]^{3+}$ and $[Os(NH_3)_4]^{2+}$. The gas-phase geometries and energies of the complexes, in both singlet and triplet states, were computed using mostly density functional theory (DFT), while solvation effects on the energies were estimated using simple dielectric continuum methods. As spin−orbit coupling is expected to play an important role with regard to the singlet−triplet energy separation, we also undertook the ab initio calculation of spin−orbit energy corrections for a number of osmium-containing species: triplet $[Os(NH_3)_4]^{2+}$, $[Os(NH_3)_4H]^{3+}$, and $[Os(NH_3)_4H(H_2O)]^{3+}$, Os atom and its ions Os^{n+} ($n = 1 - 4$), as well as $[Os(H_2O)_6]^{3+}$. On the basis of these calculations, we expect to be able to provide realistic estimates of spin−orbit coupling contributions to the singlet−triplet splittings in our systems of interest.

Computational Methods

The calculations reported in this paper were performed using density functional theory (DFT) utilizing the B3P86 hybrid functional,[5,6] which consists of the local (spin) density approximation with the Dirac exchange term (LDA), SCF, and Becke's B88X exchange (X) functionals[6] and the Vosko, Wilk, Nusair[7] (VWN), and Perdew's P86 correlation (C) functionals,[5] as defined by

$$E_{XC} = (1 - 0.2)E_X^{LDA} + 0.2E_X^{HF} + E_C^{VWN} + 0.72E_X^{B} + 0.81E_C^{P86} \quad (1)$$

The effective core potentials (ECPs) and basis sets reported by Stoll et al.[8,9] were used for the heavy atoms. Thus, the valence basis for Os is a [6s5p3d] set to accommodate the valence 5s, 5p, and 5d electrons; for C, N, O, Cl, and H, it is a double-ζ set, [2s2p] and [2s] for the heavy atoms and H, respectively. In the case of the hydrogen directly bonded to osmium, the H basis is extended by a set of p polarization functions with exponent 0.8. The geometries were fully optimized at the DFT(B3P86) level; where appropriate, the second derivatives and harmonic frequencies were also computed. The charge distributions of the complexes were analyzed by the Roby−Davidson[10−13] method.

As a test of the sensitivity of the geometries and energetics to the choice of method, the geometries of $[Os(NH_3)_4H\ H_2O]^{3+}$ were also optimized using the MP2 method. Single-point energies were then computed at the MP4 level (at the MP2 geometries) and also using the B3LYP, B3PW91, and BLYP functionals (at the B3P86 geometries). To explore the validity of the single reference treatment in SCF, CASSCF calculations were also carried out (at B3P86 geometries), with six active electrons in an active space of seven orbitals. The results obtained in these studies were found to be in good agreement with those from the B3P86 calculations.

The adequacy of the valence double-ζ basis used for the ligands was checked by comparing the geometries and energies obtained for $[Os(NH_3)_5H]^{3+}$ and $[Os(NH_3)_5(H)CH_3OH]^{3+}$ with those obtained by calculations that use the 6-31G(d,p) basis set on the ligand atoms. As will be discussed later, use of the larger basis sets results in essentially negligible changes in geometries and relatively small changes in the singlet−triplet energy differences.

Solvation energies were calculated using the isodensity-polarized continum model[14] (IPCM), where the solute/solvent interaction is calculated by a dielectric continuum approach. The cavity occupied by the solute is defined by an isodensity surface (4×10^{-4} e/a_0^3) of the molecule, which is determined by an iterative self-consistent process. Application of the IPCM method has, however, necessitated all electron calculations; these were performed at the ECP-optimized geometries, the core orbitals of each atom expanded in terms of Huzinaga's minimal basis sets.[15]

The spin−orbit interaction energies were computed by application of the Pauli−Breit spin−orbit coupling operator in a basis of Russell−Saunders states,[16−18] computed by full configuration interaction (CI) in an active space, as implemented in the fully optimized reaction space (FORS) method of Ruedenberg and co-workers.[19−22] The FORS CI calculations in our work generally include the nonbonding d electrons of osmium as well as a number of the highest energy bonding electrons distributed among a set of molecular orbitals (MOs) that include the 5d, 6s, and 6p metal orbitals. The MOs were usually generated by the open-shell restricted Hartree−Fock (ROHF) and generalized valence bond methods,[23] ensuring unitary invariance among the degenerate sets of open-shell MOs. The basis sets used are those utilized in the IPCM computations.

All DFT, MP2, and MP4 computations were carried out using the Gaussian94 and 98 programs.[24−25] The spin−orbit coupling calculations were performed using the GAMESS codes.[26]

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Table 1. Hybridization Schemes and Expected Geometries for Singlet- and Triplet-State Complexes of Os(II) and Os(IV)

	Os(II)		Os(IV)	
no. of ligand	singlet	triplet	singlet	triplet
2	d^2, ds (angular)	ds (angular)	d^2, ds (angular)	d^2, ds (angular)
3	d^2s (trigonal planar)	dsp (planar)	d^3, d^2s (trigonal planar)	d^2s (trigonal planar)
4	d^2sp	dsp^2 (tetragonal)	d^3s (tetrahedral)	d^2sp
5	d^2sp^2 (tetragonal pyramid)	dsp^3 (bipyramid)	d^3sp (bipyramid)	d^2sp^2 (tetragonal pyramid)
6	d^2sp^3 (octahedral)		d^3sp^2	d^2sp^3 (octahedral)
7			d^3sp^3	

Qualitative Molecular Orbital Theory of Os(II) and Os(IV) Complexes

Before a discussion of the geometries and energetics of the complexes studied in this work, it is useful and instructive to construct a simple qualitative molecular orbital model for the various Os(II) and Os(IV) systems but which, in reality, is based on Pauling's valence bond (VB) model of transition metal complexes.

According to ligand field theory, as applied to these complexes, the bonding and antibonding σ-type MOs are constructed from the 5d, 6s, and 6p atomic orbitals (AOs) of the metal ion and the appropriate ligand MOs containing the lone pairs of electrons that will occupy the bonding MOs of the complex. The six and four d electrons of Os^{2+} and Os^{4+}, respectively, occupy the nonbonding 5d AOs of the metal. Therefore, an Os(IV) low-spin singlet complex must have at least two nonbonding 5d AOs, while a triplet-state complex needs at least three nonbonding 5d AOs, allowing the remaining three and two 5d AOs, respectively, to contribute to bonding (and antibonding) MOs. Since the energy difference between the nonbonding and antibonding MOs in the higher transition metal complexes is generally quite large, we can effectively rule out the occupancy of the latter in ground-state configurations. Thus, while in a six-coordinate complex of Os(IV) (with three nonbonding 5d AOs) the singlet and triplet configurations would have comparable energies, the ground state of a six-coordinate Os(II) complex is certain to be a singlet, as is, indeed, found experimentally. Assuming that the number of metal AOs needed to form the bonding MOs is equal to the number of ligands, i.e., the number of σ MOs with ligand lone pairs, we can predict the maximum coordination numbers of Os(II) and Os(IV) and possibly even the resulting geometries by considering what type of hybrid orbitals can be formed from the available 6s, 5d, and 6p AOs. This is effectively equivalent to applying Pauling's VB description to the bonding,[27] whereby each metal−ligand bond is a localized two-center MO constructed from a metal hybrid and a ligand σ orbital. Allowing for interaction among the localized bonding MOs then results in symmetry-adapted delocalized bonding MOs. Note, however, that in principle one could obtain a sufficient number of bonding MOs by using a smaller number of metal AOs than the number of ligands, as in the MO description of electron-rich molecules such as SF_6, but whether this would be viable for the systems of interest here could only be answered by actually carrying out the MO computations. To determine the most likely type of hybrid orbitals we make a further assumption, in that 6p Os AO participation is kept at a minimum level, since that AO has a significantly higher energy than the 6s and 5d AOs. The resulting plausible hybridization schemes for 2−7 ligands for Os(II) and Os(IV), taken from the tabulation of Eyring, Walter, and Kimball,[28] are given in Table 1, along with the corresponding geometries. The d^2sp, d^3sp^2, and d^3sp^3 hybrids do not correspond to symmetric arrangement—they are labeled "irregular tetrahedron", "mixed", and "ZrF_7^{3-}," respectively, by Eyring et al.[28]

According to the above arguments, therefore, a tetracoordinate Os(II) complex would be expected to have an irregular tetrahedral structure in the singlet state, but a tetragonal, viz. square planar structure in the triplet state. A pentacoordinate Os(IV) complex is expected to be bipyramidal in the singlet state, while the triplet would be a tetragonal pyramid. Octahedral structures are expected for six-coordinate singlet Os(II) and triplet Os(IV) complexes, while a singlet Os(IV) complex, utilizing d^3sp^2 hybrid orbitals, is expected to have a more irregular or "mixed"-type structure. No six-coordinate or seven-coordinate triplet Os(II) complex is expected to exist, but seven-coordinate singlet Os(IV) would be allowed. (The pentagonal bipyramidal structure that has been proposed for $[Os(bpy)(PPh_3)_2(CO)H_2]^{2+}$ by Sullivan et al.[3] is consistent with a ZrF_7^{3-}-type structure.) As will be shown in the following section, these predictions are largely confirmed by the calculations. The following question then arises: What are the apparently seven-coordinate Os(IV) complexes observed by Li, Yeh and Taube[1]? There are two possibilities: (a) six metal AO's, along with seven ligand σ orbitals, are adequate for the formation of the bonding MOs to accommodate the 14 electrons, (b) the complex is really six-coordinate with an additional ligand in the second coordination shell but strongly bound to the actual complex. As discussed in the next section, the DFT calculations support the second alternative.

Geometries

The optimized (gas-phase) structures of the $[Os(NH_3)_4H(L_1^x)_m(L_2^y)_n]^{(mx+ny+3)+}$ complexes with H_2O as the ligands L_1^x and L_2^y, along with those of the parent systems $[Os(NH_3)_4H]^{3+}$ and $[Os(NH_3)_4]^{2+}$, in their singlet and triplet states, are shown in Figures 1 and 2, respectively.

The structures of the singlet-state systems (Figure 1) conform in an approximate sense to the predictions based on hybridiza-

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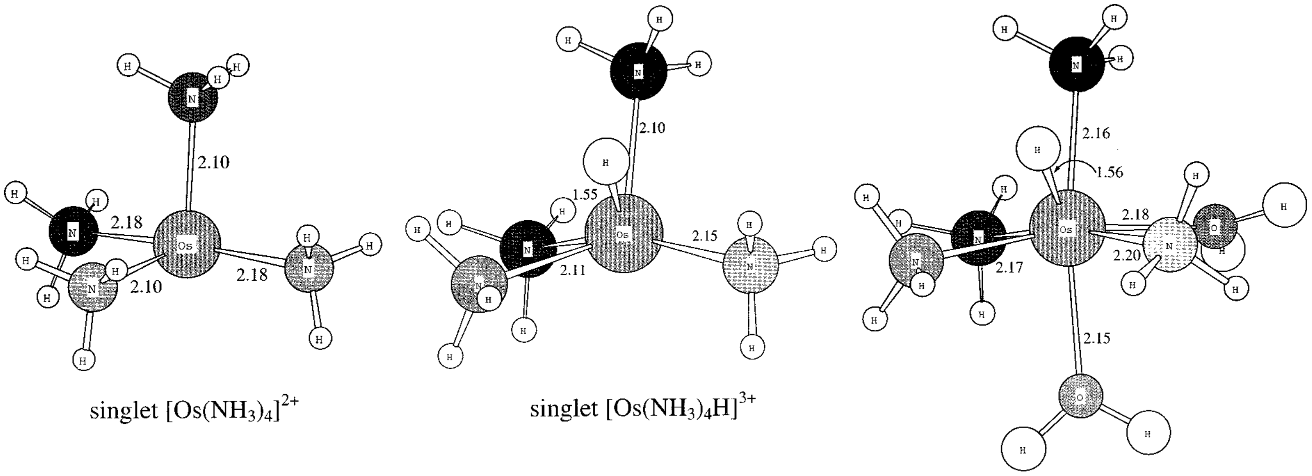
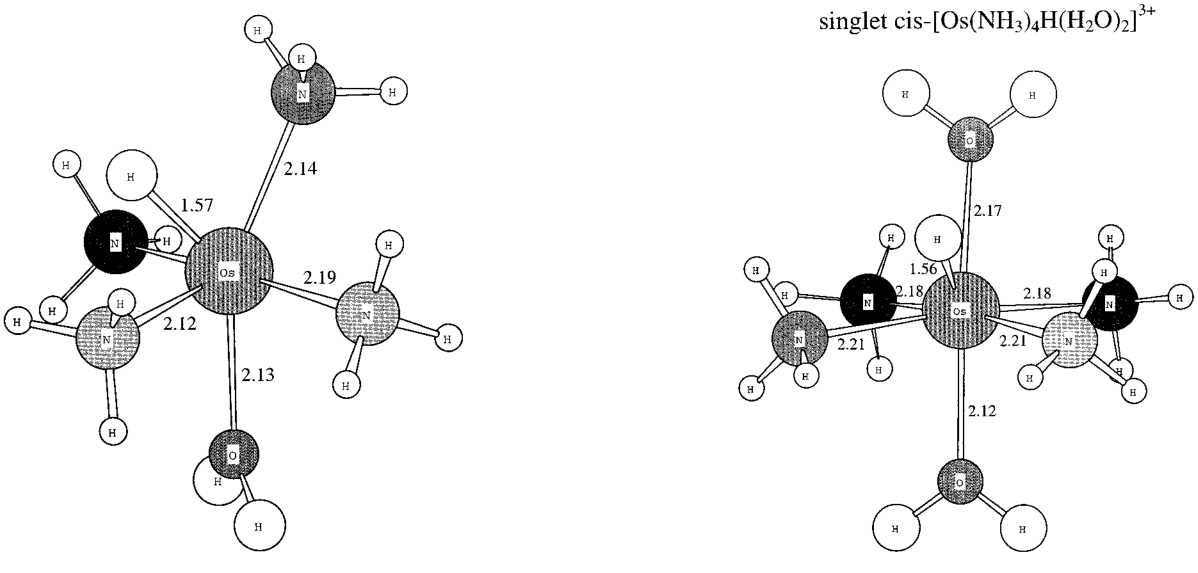


singlet $[Os(NH_3)_4]^{2+}$ singlet $[Os(NH_3)_4H]^{3+}$ singlet cis-$[Os(NH_3)_4H(H_2O)_2]^{3+}$



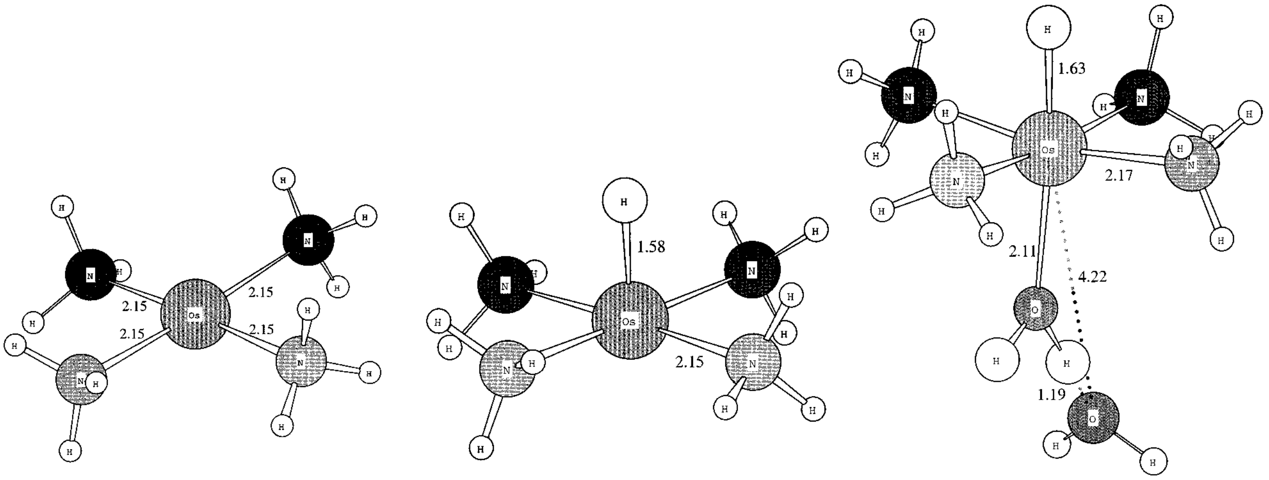
singlet $[Os(NH_3)_4H(H_2O)]^{3+}$ singlet trans-$[Os(NH_3)_4H(H_2O)_2]^{3+}$

Figure 1. Structures of singlet $[Os(NH_3)_4]^{2+}$, $[Os(NH_3)_4H]^{3+}$, $[Os(NH_3)_4H(H_2O)]^{3+}$, and $[Os(NH_3)_4H(H_2O)_2]^{3+}$ complexes.

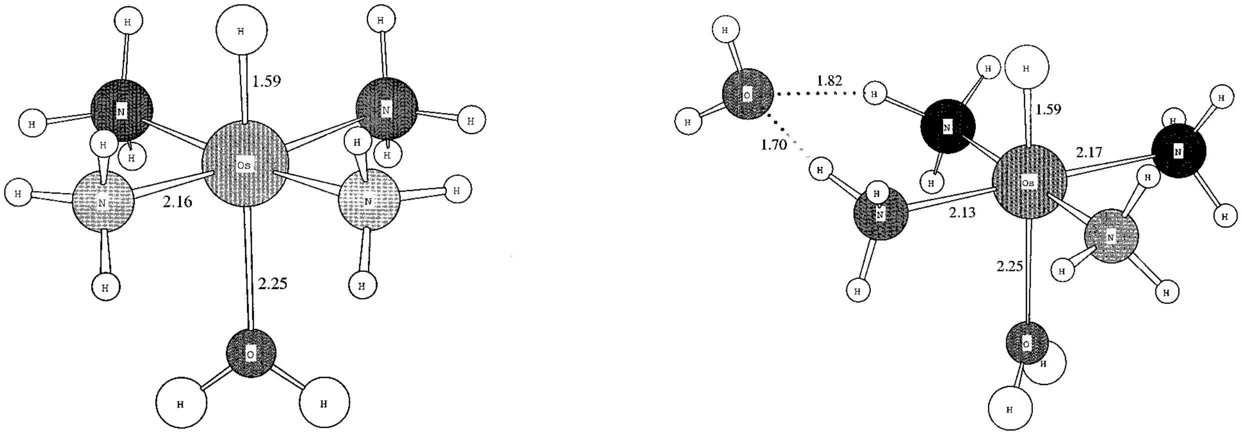
tion, as outlined in the previous section. $[Os(NH_3)_4]^{2+}$ can be described as an irregular tetrahedron, although it is better characterized in terms of two sets of hybrids, ds and dp, which are a pair with a 90° angle (formed from $d_{x^2-y^2}$ and s AOs) and a linear pair perpendicular to the former pair (formed from d_{z^2} and p_z AOs). $[Os(NH_3)_4H]^{3+}$ can be regarded as a distorted trigonal bipyramid. Alternatively, it can be described as being based on the $[Os(NH_3)_4]^{2+}$, with the Os−H bond formed by the overlap of the hydrogen 1s AO with a metal d_{xy} AO. The six-coordinate species, $[Os(NH_3)_4H(H_2O)]^{3+}$, can be described as $[Os(NH_3)_4]^{2+}$ plus the bonding of H^- and H_2O to osmium by utilizing dp hybrids (formed from d_{xy} and p_x AOs). The two seven-coordinate structures, in which the water molecules are cis and trans to each other, respectively, are best described as octahedral $[Os(NH_3)_4(H_2O)_2]^{2+}$, i.e., with d^2sp^3 hybridization on Os, plus a hydride, where the Os−H bond is formed by the overlap of the H 1s AO with a metal orbital which is a combination d_{xz} and d_{yz} AOs. The structures can be seen to conform to the distorted trigonal prism-derived structure of ZrF_7^{3-}.

The structures of the triplet-state molecules (Figure 2) are entirely as expected on the basis of the qualitative MO arguments and the appropriate hybridization of the osmium AOs. Thus, $[Os(NH_3)_4]^{2+}$ is square planar (as required by the dsp^2 hybridization), and $[Os(NH_3)_4H]^{3+}$ has a tetragonal pyramidal structure (consistent with d^2sp^2 hybridization), while $[Os(NH_3)_4H(H_2O)]^{3+}$ is octahedral (with d^2sp^3 hybridization). Two distinct structures were located for triplet $[Os(NH_3)_4H(H_2O)_2]^{3+}$, called cis and trans, where the naming, while appropriate for the starting structures in the geometry optimization process, is less apt for the resulting equilibrium geometries. The two structures are best described as octahedral $[Os(NH_3)_4H(H_2O)]^{3+}$ with a second water molecule in the second coordination shell which is hydrogen bonded to the first water or to two ammonias. This finding is also consistent with the MO argument that the maximum coordination of Os(IV) in a triplet state is expected to be six.

Replacing the two water molecules with ammonia and methanol as the ligands L_1 and L_2, yielded the structures shown in Figures 3 and 4 for the singlet- and triplet-state molecules. The similarities between these structures and those of water-containing complexes are quite evident, although the structure of $[Os(NH_3)_5H]^{3+}$ is best described in terms of dsp^2 hybridization (that yields the tetragonal arrangement of the first four ammonias), plus the formation of Os−H and $Os-NH_3$ bonds by utilizing the d_{xz} and d_{yz} AOs of Os. Again, an unambiguously seven-coordinate structure is found only for the singlet-state molecule. In the triplet-state system, methanol is hydrogen bonded to two ammonia ligands of the six-coordinate, nearly octahedral $[Os(NH_3)_5H]^{3+}$. We propose, therefore, that this is

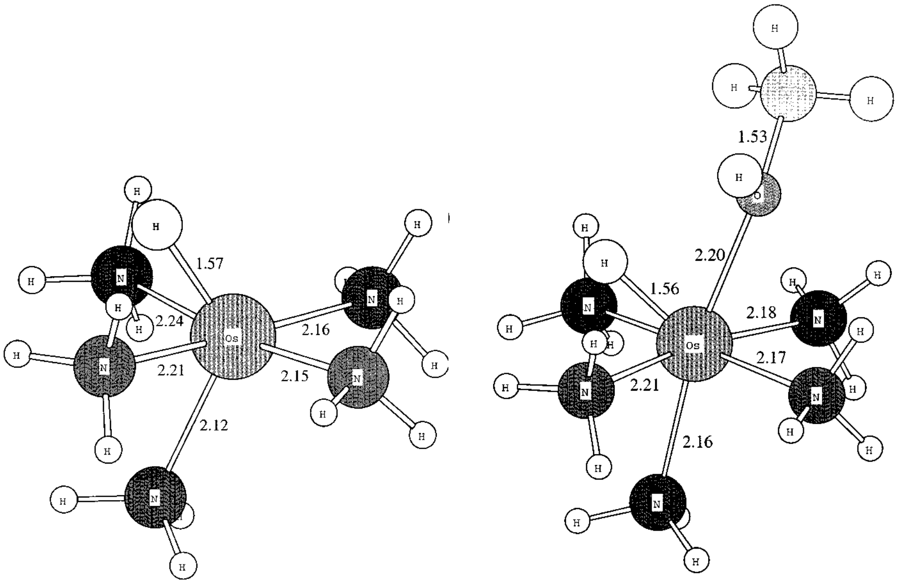


triplet $[Os(NH_3)_4]^{2+}$ triplet $[Os(NH_3)_4H]^{3+}$ triplet cis-$[Os(NH_3)_4H(H_2O)_2]^{3+}$



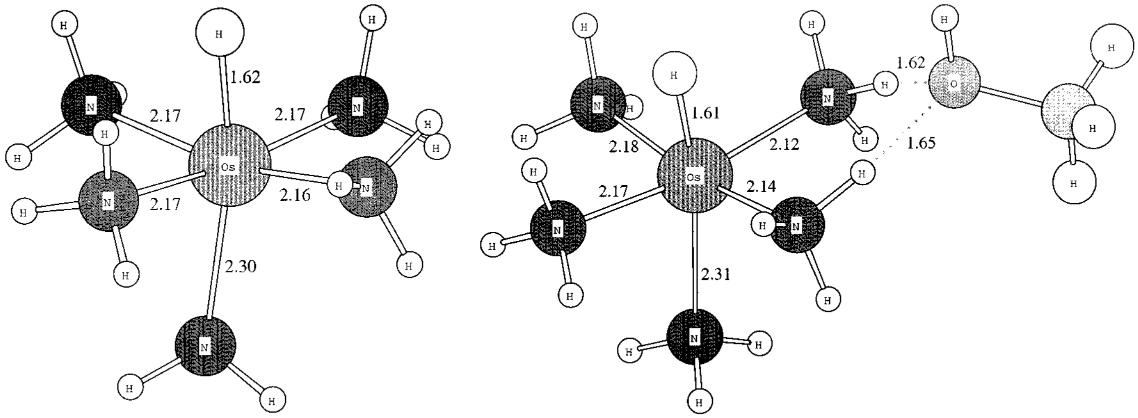
triplet $[Os(NH_3)_4H(H_2O)]^{3+}$ triplet trans-$[Os(NH_3)_4H(H_2O)_2]^{3+}$

Figure 2. Structures of triplet $[Os(NH_3)_4]^{2+}$, $[Os(NH_3)_4H]^{3+}$, $[Os(NH_3)_4H(H_2O)]^{3+}$, and $[Os(NH_3)_4H(H_2O)_2]^{3+}$ complexes.



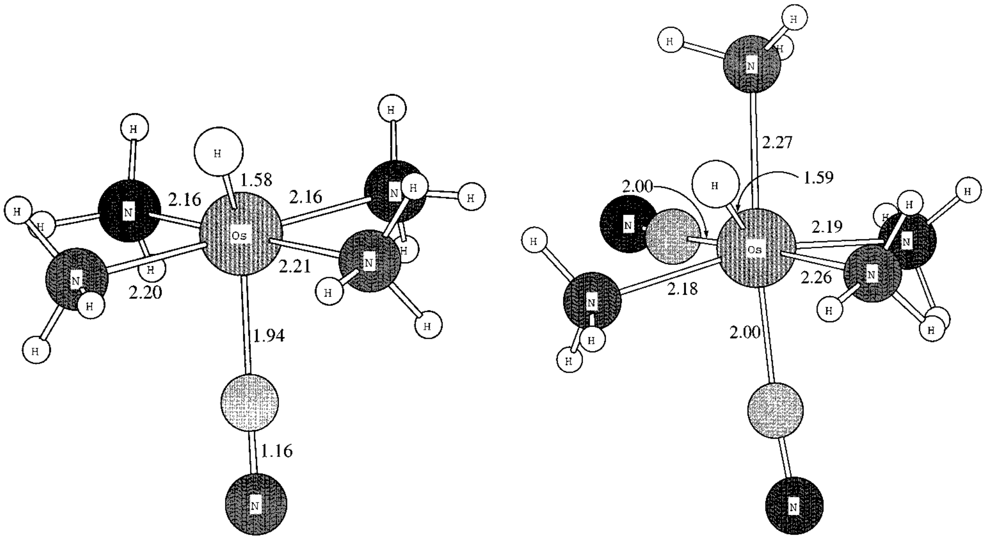
singlet $[Os(NH_3)_5H]^{3+}$ singlet $[Os(NH_3)_5H(CH_3OH)]^{3+}$

Figure 3. Structures of singlet $[Os(NH_3)_5H]^{3+}$ and $[Os(NH_3)_5H(CH_3OH)]^{3+}$ complexes.



triplet $[Os(NH_3)_5H]^{3+}$ triplet $[Os(NH_3)_5H(CH_3OH)]^{3+}$

Figure 4. Structures of triplet $[Os(NH_3)_5H]^{3+}$ and $[Os(NH_3)_5H(CH_3OH)]^{3+}$ complexes.



singlet $[Os(NH_3)_4H(CN)]^{2+}$ singlet $[Os(NH_3)_4H(CN)_2]^{2+}$

Figure 5. Structures of singlet $[Os(NH_3)_4H(CN)]^{2+}$ and $[Os(NH_3)_4H(CN)_2]^{+}$ complexes.

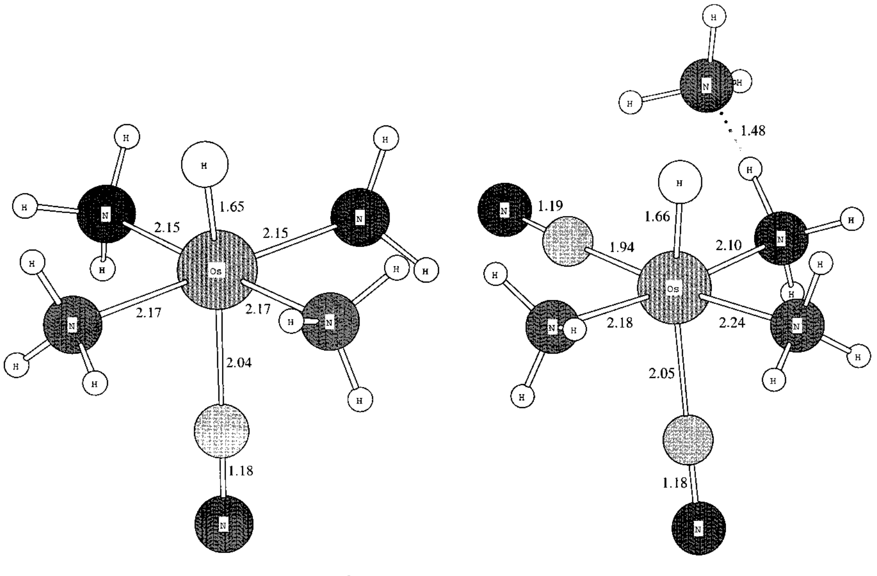
the structure of the $[Os(NH_3)_5H(CH_3OH)]^{3+}$ ion observed by Li, Yeh, and Taube.[1]

In essence, our findings for the remaining systems, where the ligands L_1 and L_2 in the six- and seven-coordinate Os(IV) complexes are cyanide (Figures 5 and 6), chloride (Figures 7 and 8), and acetonitrile (Figures 9 and 10), are the same as for those discussed above. Irrespective of the choice of ligands, plausible seven-coordinate species could be identified only for singlet-state systems. In none of the corresponding triplet-state molecules can the seventh ligand be described as bonded to the osmium. Indeed, in the case of triplet $[Os(NH_3)_4H(CH_3CN)_2]^{3+}$, the (gas-phase) geometry optimization was initially converging to a structure with one ammonia molecule in the second coordination shell, i.e., hydrogen bonded to a hexacoordinate $[Os(NH_3)_4H(CH_3CN)_2]^{3+}$. However, that structure turned out to be a saddle point on the potential energy surface, and on further optimization proton transfer took place, yielding in effect the ion pair $[Os(NH_3)_3(NH_2)H(CH_3CN)_2]^{2+}\cdots NH_4^{+}$, which then proceeded to dissociate. It is possible that solvation could stabilize the hydrogen-bonded system, but unfortunately geometry optimization of a solvated structure is outside the scope of our computing resources. The geometry shown in Figure 10, chosen somewhat arbitrarily for subsequent studies of the relative stabilities of the singlet and triplet isomers, represents the lowest energy structure of this system, where the NN distance (2.82 Å) in the $H_2N^{-}\cdots HNH_3^{+}$ fragment is consistent with the existence of a hydrogen bond between the amide and ammonium moieties. A number of different structures were experimented with in an effort to find a low-energy, stable geometry for the triplet state, but they appeared to converge to the one discussed above or to higher energy structures which also dissociated.

As a test of our computational protocol, the geometries of $[Os(NH_3)_5H]^{3+}$ and $[Os(NH_3)_5H(CH_3OH)]^{3+}$ were recomputed, using larger basis sets for the ligands, namely the 6-31G(d) and 6-31G(d,p) sets, respectively, for the two systems. The changes in geometry, as expected, were found to be negligible. The energy changes accompanying the geometry relaxations were found to range from ~1 to ~4 kcal mol^{-1}.

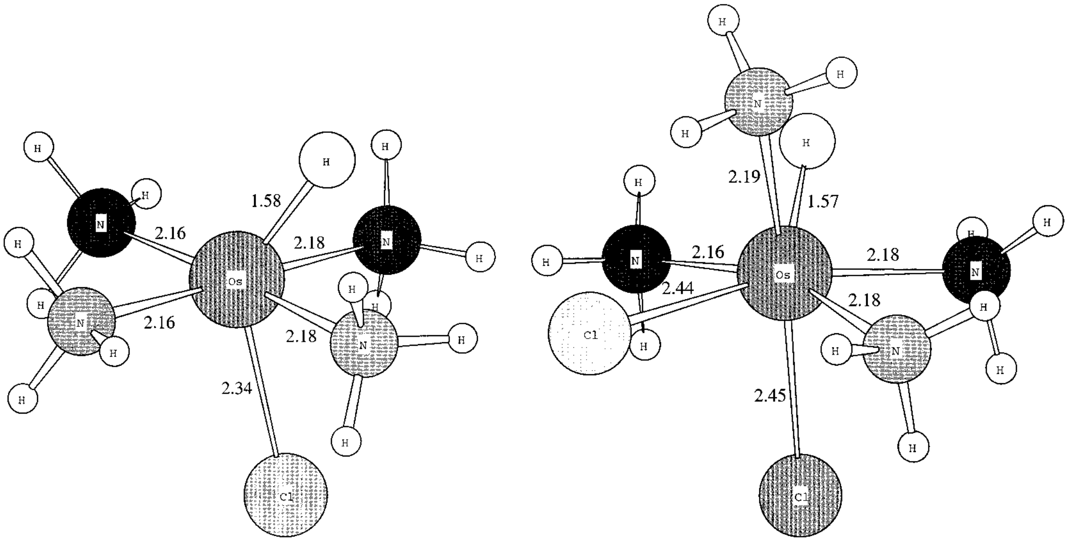
Spin−Orbit Coupling

Spin−orbit coupling calculations, as described in the Computational Methods section, were carried out for the Os atom and its ions Os^{n+} ($n = 1-4$), triplet $[Os(NH_3)_4]^{2+}$, $[Os(NH_3)_4H]^{3+}$, and $[Os(NH_3)_4H(H_2O)]^{3+}$, as well as $[Os(H_2O)_6]^{3+}$, at their computed equilibrium geometries. The results are summarized in Table 2, which lists the energy of the most stable



triplet $[Os(NH_3)_4H(CN)]^{2+}$ triplet $[Os(NH_3)_4H(CN)_2]^{2+}$

Figure 6. Structures of triplet $[Os(NH_3)_4H(CN)]^{2+}$ and $[Os(NH_3)_4H(CN)_2]^{+}$ complexes.



singlet $[Os(NH_3)_4H(Cl)]^{2+}$ singlet $[Os(NH_3)_4H(Cl)_2]^{+}$

Figure 7. Structures of singlet $[Os(NH_3)_4H(Cl)]^{2+}$ and $[Os(NH_3)_4H(Cl)_2]^{+}$ complexes.

Table 2. Computed Spin−Orbit Coupling Corrections to the Ground-State Energies of Selected Ions and Complexes (in cm^{-1})

system	$-\Delta E_{SO}$
Os (^{5}D)	2142
Os$^+$ (^{6}D)	1833
Os^{2+} (^{5}D)	2640
Os^{3+} (^{6}S)	712
Os^{4+} (^{5}D)	4720
$[Os(NH_3)_4]^{2+}$ (^{3}E)	2425
$[Os(NH_3)_4H]^{2+} = [Z]^{3+}$ (^{3}E)	1563
$[Z\text{-}(H_2O)]^{3+}$ (^{3}E)	2080
$[Os(H_2O)_6]^{2+}$ ($^2T_{2g}$)	2915

spin-orbit coupled state relative to the degenerate adiabatic ground state. With the exception of Os^{3+} (where spin−orbit coupling in the ^{6}S state arises as a result of admixture with excited P, D, etc. states), the energetic stabilization due to spin−orbit coupling is generally ~2000−3000 cm^{-1} (5.7−8.6 kcal mol^{-1}), although for Os^{4+} it is computed to be considerably larger.

Direct comparison with experiment is possible in the case of Os and Os$^+$, for which accurate gas-phase spectroscopic data are available.[29] The computations for Os and its ions (that include a range of quintet and triplet configurations in the spin−orbit coupling calculations) yielded energies for all J values which conform to the Landé interval rule[30] reasonably well, as may be expected on the basis of Russell−Saunders coupling. Thus, for the ...6s^{2}5d^6 (^{5}D), the computed energies for $J = 4$, 3, 2, 1, and 0 are (relative to the energy of $J = 4$) 0, 2075, 3136, 3926, and 4323 cm^{-1} (which would yield spin−orbit coupling constants of 519, 354, 395, and 397 cm^{-1}). However, the corresponding experimental energies are 0, 4159, 2740, 5766, and 6093 cm^{-1}, which do not conform to the Landé interval rule at all. Thus, with regard to individual energies, the calculations compare very poorly with experiment. Similar

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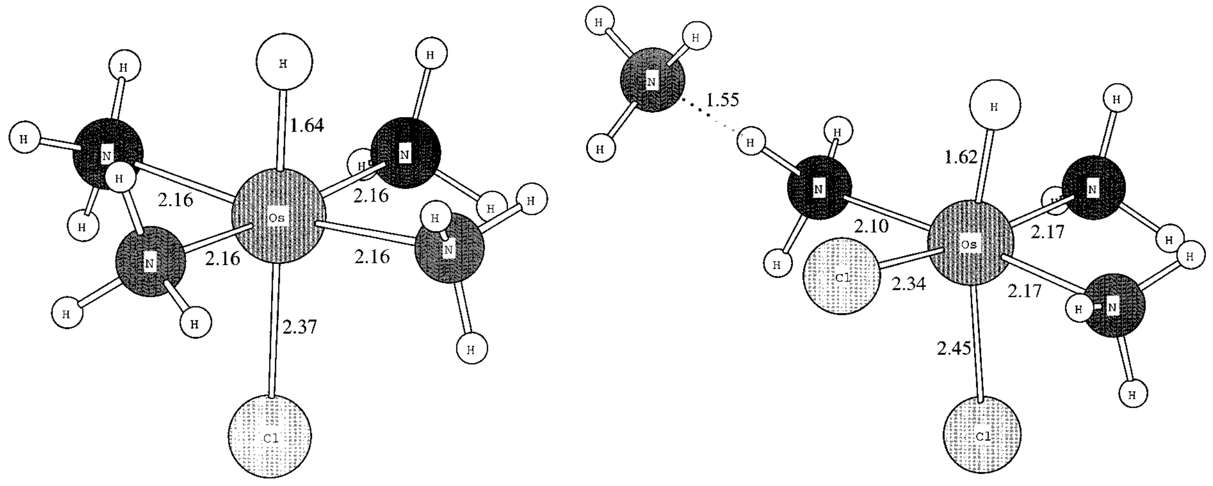
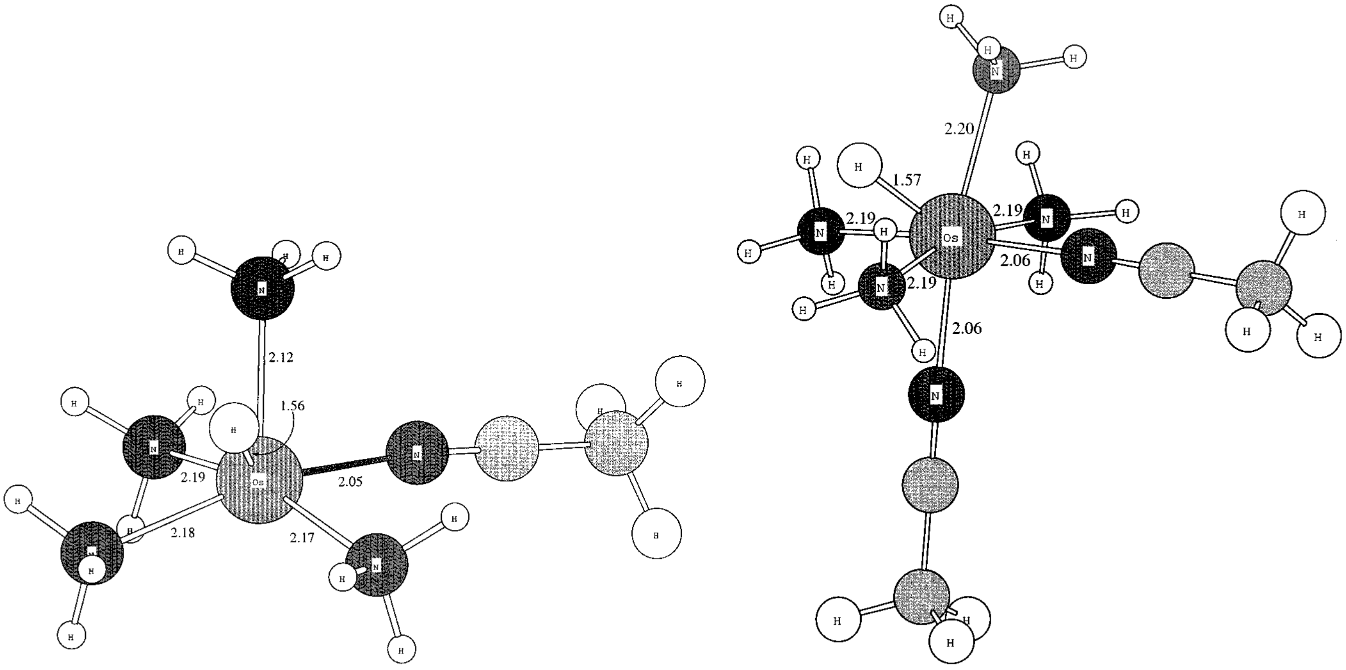
[29] Moore, C. E. *Atomic Energy Levels*; Circular of the National Bureau of Standards 467; U.S. Government Printing Office: Washington, DC, 1958; Vol. III.

[30] Condon, E. U.; Shortley, G. H. *The Theory of Atomic Spectra*; Cambridge University Press: Cambridge, 1951; p 195.



triplet $[Os(NH_3)_4H(Cl)]^{2+}$ triplet $[Os(NH_3)_4H(Cl)_2]^{+}$

Figure 8. Structures of triplet $[Os(NH_3)_4H(Cl)]^{2+}$ and $[Os(NH_3)_4H(Cl)_2]^{+}$ complexes.

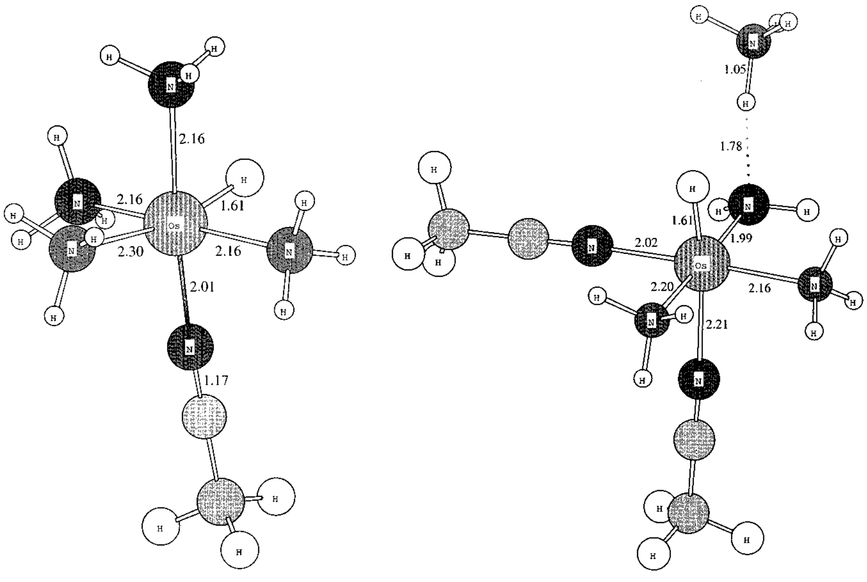


singlet $[Os(NH_3)_4H(CH_3CN)]^{3+}$ singlet $[Os(NH_3)_4H(CH_3CN)_2]^{3+}$

Figure 9. Structures of singlet $[Os(NH_3)_4H(CH_3CN)]^{2+}$ and $[Os(NH_3)_4H(CH_3CN)_2]^{+}$ complexes.

discrepancies are evident for the ...$6s^15d^7$ (^5F) state of Os and the ...$6s^15d^6$ (^6D) state of Os^+. Clearly, the use of the Russell–Saunders coupling scheme for free Os and its ions is inadequate; i.e., our limited CI computations do not include a sufficient number of states to reproduce what is best described in terms of *jj* coupling. A less exacting comparison would compare the total spread in the computed energies, which for Os (^5D) is 4323 cm^{-1}, with the experimental value of 6093 cm^{-1}. Similar or even better agreement by such criterion is found for Os (^5F) and Os^+(^6D).

With regard to the calculation of spin–orbit coupling in transition metal complexes, it is useful to keep in mind that bonding causes the quenching, to a large extent, of the orbital angular momentum of the electrons. Appreciable spin–orbit coupling can be expected to occur if the nonbonding metal d electrons occupy open-shell orbitals with nonzero angular momentum that yields a degenerate electronic state, such that on rotation about a given axis (usually taken as z) the components of the state transform into each other. Usually this is equivalent to a single electron occupying one of the degenerate pairs of orbitals d_{xz} and d_{yz} (or one of $d_{x^2-y^2}$ and d_{xy}). In the present case, triplet $[Os(NH_3)_4]^{2+}$, $[Os(NH_3)_4H]^{3+}$, and $[Os(NH_3)_4H(H_2O)]^{3+}$ are of C_{4v} symmetry, and thus the nonbonding six, four, and four electrons, respectively, occupy the degenerate d_{xz} and d_{yz} orbitals (which transform as e in C_{4v}), along with the $d_{x^2-y^2}$ and d_{z^2} orbitals (which both transform as a_1), resulting in ...$e^3a_1{}^2a_1{}^1$, ...$e^3a_1{}^1$, and $e^2b_2{}^2$ configurations, respectively. The calculations on $[Os(H_2O)_6]^{3+}$ were carried out in D_{2h} symmetry, which resulted in the d_{xy}, d_{xz}, and d_{yz} orbitals forming a triply degenerate set, while the (unoccupied) $d_{x^2-y^2}$ and d_{z^2} orbitals were also degenerate, as would be the case in full O_h symmetry. Therefore, we decided to label the above groups of orbitals t_{2g} and e_g, and thus the ground state is triply degenerate $^2T_{2g}$. Interestingly, in $[Os(NH_3)_4H(H_2O)]^{3+}$, the corresponding sets



triplet $[Os(NH_3)_4H(CH_3CN)]^{3+}$ triplet $[Os(NH_3)_4H(CH_3CN)_2]^{3+}$

Figure 10. Structures of triplet $[Os(NH_3)_4H(CH_3CN)]^{2+}$ and $[Os(NH_3)_4H(CH_3CN)_2]^{+}$ complexes.

of orbitals are, in fact, nearly degenerate. These calculations are very resource-intensive and could be carried out successfully only by the maximum utilization of symmetry. Thus, unfortunately, spin−orbit coupling calculations on $[Os(NH_3)_5H(CH_3OH)]^{3+}$ and $[Os(NH_3)_5H]^{3+}$ which have C_1 and C_s symmetries, respectively, proved too large to carry out at present. For these systems, therefore, we use the value of −5.9 kcal mol^{-1} obtained for $[Os(NH_3)_4H(H_2O)]^{3+}$ as an estimate of the spin−orbit stabilization of the triplet state.

There are no direct experimental data on these complexes with which our computed spin−orbit energies could be compared. However, an analysis of the polarized crystal spectrum of a tris-acetyl acetone complex, carried out by Dingle,[31] suggests, on the basis of the observed (D_3) trigonal splittings, that in the higher O_h symmetry, spin−orbit coupling would split the $^2T_{2g}$ ground state into a doublet at −3150 cm^{-1} and a quartet at 1575 cm^{-1}. The inferred spin−orbit stabilization of the ground state agrees well with our calculated value of −2915 cm^{-1}, but our computed spin−orbit splitting is only 3493 cm^{-1}, i.e., 74% of the experimentally derived value.

Spin−orbit coupling is expected to have a significantly smaller effect on the energies of singlet states, especially if the energetic separations between the singlet and higher spin states are large. Our calculations on singlet $[Os(NH_3)_4]^{3+}$, $[Os(NH_3)_4H]^{3+}$, and $[Os(NH_3)_4H(H_2O)]^{3+}$ at their DFT-optimized geometries yielded spin−orbit energies of the order of ∼10 cm^{-1} or less.

On the basis of these calculations, we may conclude that, although a quantitative prediction of spin−orbit coupling effects for these large and complex systems has not been achieved, the computed energetic stabilizations to the triplet states may be expected to have a ∼70% accuracy.

Energetics and Stabilities

The relative energies of the above complexes in their singlet and triplet states, in the gas phase and in aqueous solution, are summarized in Table 3. The corresponding total electronic energies, individual solvation energies, and zero-point energies that were obtained at the computed DFT(B3P86) geometries are listed in Tables S1 and S2 of the Supporting Information. In the case of the four- and five-coordinate parent complexes, $[Os(NH_3)_4]^{2+}$ and $[Os(NH_3)_4H]^{3+}$, respectively, the triplet states are predicted to be distinctly more stable in the gas phase. Among the six-coordinate complexes, the triplets are marginally the more stable electronic states when $L_1 = H_2O$, NH_3, and Cl^-, but solvation appears to reverse this trend somewhat, as for most systems solvation favors the singlet states. On the other hand, when $L_1 = CN^-$ and CH_3CN, the ground state appears to be singlet. However, the addition of one more ligand to yield the seven-coordinate complexes results in singlet ground states in every case. Moreover, as our test calculations on $[Os(NH_3)_5H]^{3+}$ and $[Os(NH_3)_5H(CH_3OH)]^{3+}$ suggest, use of larger polarized bases on the ligands may further favor the singlet states.

Table 3. Singlet−Triplet Energy Differences ($\Delta E = E_{\text{singlet}} - E_{\text{triplet}}$), Calculated in the Gas Phase and in Aqueous Solution via the B3P86 Functional and the IPCM Solvation Model, for $[Os(NH_3)_4HL_1L_2]$ Complexes and Including Spin−Orbit Coupling Correction for Selected Molecules (All in kcal mol^{-1})

molecule[a]	gas phase[b]	solution[b]	solution[b] + spin−orbit correction
$[Os(NH_3)_4]^{2+}$	16.1	14.2	21.2
$[Os(NH_3)_4H]^{3+} = [Z]^{3+}$	15.7	10.7	15.2
$[Z\text{-}(H_2O)]^{3+}$	7.9	0.6	6.5
$[Z\text{-}(H_2O)_2]^{3+}$ (cis)	2.6	−15.7	−9.8
$[Z\text{-}(H_2O)_2]^{3+}$ (trans)	−0.1	−10.2	−4.3
$[Z\text{-}(NH_3)]^{3+}$	4.0 (1.4)[d]	0.7	6.6[c]
$[Z\text{-}(NH_3)(CH_3OH)]^{3+}$	−7.6 (−13.5)[e]	−4.2	1.7[c]
$[Z\text{-}CN]^{2+}$	−16.2	−9.5	
$[Z\text{-}(CN)_2]^{+}$	−23.0	−38.8	
$[Z\text{-}Cl]^{2+}$	10.8	12.6	
$[Z\text{-}(Cl)_2]^{+}$	−12.7	−21.0	
$[Z\text{-}(CH_3CN)]^{3+}$	3.4	−10.0	
$[Z\text{-}(CH_3CN)_2]^{3+}$	−13.7	−28.1	

[a] Z = $[Os(NH_3)_4H]$. [b] Including zero-point energy corrections. [c] Estimated value (using spin−orbit correction computed for $[Z\text{-}(H_2O)]^{3+}$ (−5.9 kcal mol^{-1})). [d] With 6-31G(d) basis on ligands. [e] With 6-31G(d,p) basis on ligands.

As noted above, in most cases solvation appears to favor the singlet states which are generally more compact structurally than their triplet counterparts. This shows up in the volumes of the

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[31] Dingle, R. *J. Mol. Spectrosc.* **1965**, *18*, 276.

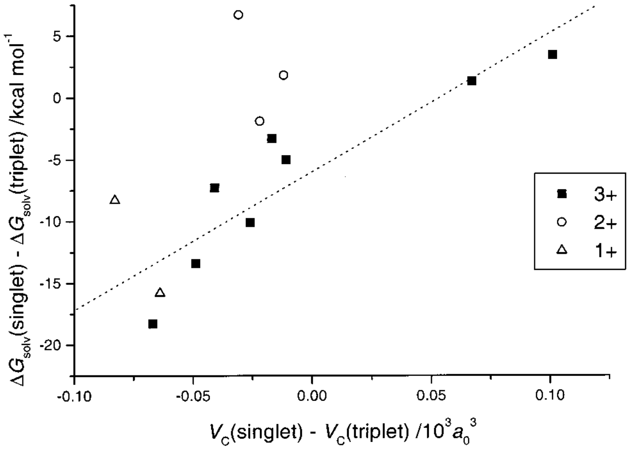

Figure 11. Correlation of singlet−triplet solvation free energy difference with difference of cavity volumes. The dotted line is a linear fit to the 3+ ion data.

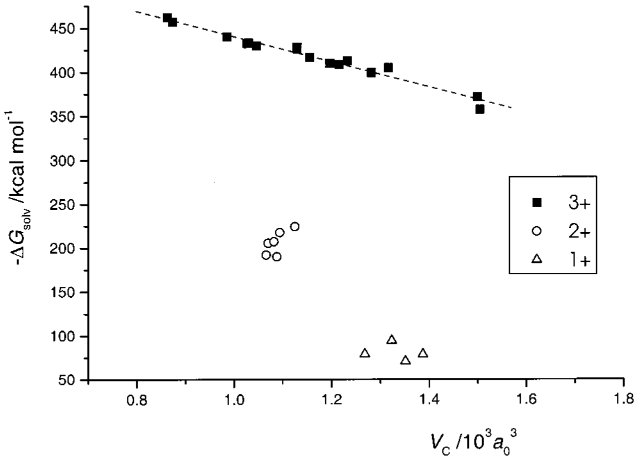

Figure 12. Correlation of the solvation free energies of the complexes with their cavity volumes. The dotted line is a linear fit to the 3+ ion data.

cavities in the dielectric continuum which accommodate the solute (determined by the IPCM computations) and which directly depend on the molecular volumes. Indeed, the plot of the singlet−triplet difference in solvation energy against the difference in cavity volumes, shown in Figure 11, indicates a degree of correlation for ions with 3+ charge. The significant contribution of solvation to the singlet−triplet energy separation, which can be as large as ∼18 kcal mol^{-1} in 3+ ions, should be noted. This suggests that, to a large extent, the magnitude of the solvation energy in each system is dominated by the Born term, i.e., by the interaction of the net charge with the dielectric representing the solvent.[32−34] As a further illustration of this behavior, a plot of computed solvation energies of all the molecules studied in this work against their respective computed cavity volumes is shown in Figure 12. Depending on the net charge, the plotted points fall into one of three distinct groups. The expected correlation between the free energy of solvation and cavity volumes is clearly displayed by molecules with 3+ charge but hardly, if at all, by molecules with 2+ and 1+ charges. The situation is obviously more complex for the latter systems, especially as no obvious correlation between solvation energies and dipole moments was found either. This suggests that a simple Onsager-type SCRF model[33,34] of solvation would be inadequate for these systems. As according to the Born model of solvation,[32] the free energy of solvation ΔG_{solv} of an ion with charge Z in a spherical cavity of radius R_C in a dielectric continuum with dielectric constant ϵ is

$$\Delta G_{solv} = -\left(1 - \frac{1}{\epsilon}\right)\frac{Z^2}{2R_C} \qquad (2)$$

a correlation between solvation energy and $Z^2V_C^{-1/3}$ (where V_C is the cavity volume) could be expected. We found that, indeed, eq 2 was able to predict the solvation energies of the molecules with 3+ charge reasonably well, the average difference between the Born predictions and the IPCM computed values being ∼12 kcal mol^{-1} (∼3%), the largest deviations (21 and 35 kcal mol^{-1}) found for the singlet and triplet $[Os(NH_3)_4H(CH_3CN)_2]^{3+}$ systems, where the spherical cavity approximation may be expected to be invalid. Similarly large deviations were found for the 2+ and 1+ ions, where the Born term is no longer dominant.

Table 4. Successive Binding Energies of $L_1$and L_2 = H_2O, CH_3CN, Cl^-, and CN^- in $[Os(NH_3)_4HL_1L_2]$ Complexes (in kcal mol^{-1})[a]

		singlet		triplet	
system[b]		gas phase	solution	gas phase	solution
$[Z\text{-}(H_2O)]^{3+}$	ΔE_1	−60.1	−30.6	−52.4	−20.6
$[Z\text{-}(H_2O)_2]^{3+}$ (cis)	ΔE_2	−53.9	−34.8	−48.6	−18.5
$[Z\text{-}(H_2O)_2]^{3+}$ (trans)	ΔE_2	−48.4	−27.6	−40.5	−16.9
$[Z\text{-}(NH_3)]^{3+}$	ΔE_1	−78.8	−46.3	−67.1	−36.3
$[Z\text{-}(NH_3)(CH_3OH)]^{3+}$	ΔE_2	−58.6	−25.1	−47.1	−20.3
$[Z\text{-}(CN)]^{2+}$	ΔE_1	−393.5	−88.3	−361.6	−68.1
$[Z\text{-}(CN)_2]^{+}$	ΔE_2	−262.6	−78.7	−255.8	−49.4
$[Z\text{-}(Cl)]^{2+}$	ΔE_1	−354.7	−31.5	−349.7	−33.4
$[Z\text{-}(Cl)_2]^{+}$	ΔE_2	−230.4	−37.6	−207.0	−4.1
$[Z\text{-}(CH_3CN)]^{3+}$	ΔE_1	−97.5	−42.4	−85.2	−21.7
$[Z\text{-}(CH_3CN)_2]^{3+}$	ΔE_2	−82.8	−35.9	−65.7	−17.8

[a] Without spin−orbit corrections. [b] Z = $[Os(NH_3)_4H]$.

The inclusion of spin−orbit contributions, as discussed above, is expected to favor the triplet state systems. If we apply the spin−orbit energy correction of −5.9 kcal mol^{-1} (computed for $[Os(NH_3)_4H(H_2O)]^{3+}$) to $[Os(NH_3)_5H]^{3+}$ and $[Os(NH_3)_5H(CH_3OH)]^{3+}$, the stabilities of the triplet and singlet states would become comparable.

To establish the relative stabilities of the six- and seven-coordinate complexes, the successive binding energies, ΔE_1 and ΔE_2, of the ligands L_1 and L_2, respectively, were also computed (without spin−orbit corrections). Defined as the energies of the reactions

$$[Os(NH_3)_4H]^{3+} + L_1^{\,x} \rightarrow [Os(NH_3)_4HL_1]^{(x+3)+} \qquad \Delta E_1 \quad (3.1)$$

$$[Os(NH_3)_4HL_1]^{(x+3)+} + L_2^{\,y} \rightarrow [Os(NH_3)_4HL_1L_2]^{(x+y+3)+} \qquad \Delta E_2 \quad (3.2)$$

the computed successive binding energies are presented in Table 4. As expected, the binding energies of the ligands in solution are considerably smaller in magnitude than those in the gas phase. However, the most significant finding is that, in general, the seven-coordinate triplet-state complexes are significantly less stable in solution than their singlet counterparts. As noted already, these are complexes in which the seventh ligand is not in the first coordination shell, and such a ligand might be

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(32) Born, M. *Z. Phys.* **1920**, *1*, 45.

(33) Bacskay, G. B.; Reimers, J. R. In *Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Ed.; J. Wiley & Sons Ltd.: Chichester, 1998; p 2620.

(34) Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027.

expected to exchange with a solvating water molecule, which would be manifested in nearly zero binding energy for it in solution. In our study, such behavior is evident only in the case of the chloride complex. We note in particular that in the case of triplet $[Os(NH_3)_5CH_3OH]^{3+}$, the binding energy of methanol at ∼20 kcal mol^{-1} (Table 4) is sufficiently large that it would not be expected to rapidly exchange with solvent molecules. This is in accordance with experimental findings.[1]

The theoretical prediction that triplet $[Os(NH_3)_5CH_3OH]^{3+}$ could be stable in solution appears to be borne out by the experimental observations of Li, Yeh, and Taube,[1] although according to our work methanol is not in the first coordination shell. On the other hand, as no true equilibrium geometry was found for triplet $[Os(NH_3)_4H(CH_3CN)_2]^{3+}$ in the gas phase, the current calculations do not lead to any definite conclusions about this proposed molecule.

In summary, on the basis of these calculations, the six-coordinate complexes $[Os(NH_3)_4HL_1{}^{x}]^{(x+3)+}$, where $L_1 = H_2O$, NH_3, CH_3CN, Cl^-, and CN^-, are expected to be stable in solution, in both singlet and triplet states, while true seven-coordinate complexes are expected to be stable only as singlets. Nevertheless, due to the strong binding of the various ligands to the respective six-coordinate parent complexes, a number of triplet-state molecules that conform to the above molecular formulas are predicted to be stable, with the notable exception of $[Os(NH_3)_4H(CH_3CN)_2]^{3+}$. While spin−orbit coupling would result in increased stability for the triplet-state systems, the corrections we computed are not large enough to radically alter the above conclusions.

Li, Yeh, and Taube[1] also reported the presence of an absorption band at 1358 cm^{-1} in the infrared spectrum of solid $[Os(NH_3)_5H(CH_3OH)]\cdot 3CF_3SO_3$ which disappears on deuteration, while a new band appears at 966 cm^{-1}. Two possible assignments for this band were considered, namely Os−H stretch and symmetric deformation of bound NH_3, although neither of these was accepted by Li et al.[1] Our calculated harmonic Os−H stretch frequency in triplet $[Os(NH_3)_5H(CH_3OH)]^{3+}$ is 2189 cm^{-1}, which is much too high for this mode to be considered as a reasonable assignment. (The computed Os−H frequencies for all the systems considered in our work, ranging from 1985 to 2457 cm^{-1}, are listed in Table S1 of the Supporting Information.) The frequency of the symmetric deformation mode of the axial NH_3 (see structure in Figure 4) is 1418 cm^{-1}, which on deuteration becomes 1072 cm^{-1}. The isotopic ratio is thus too low at $1.75^{1/2}$ when compared with the experimental value of $1.99^{1/2}$. However, on the basis of our computed frequencies, we wish to propose an alternative assignment, namely that the observed frequencies correspond to OH bends in the methanol which is bound to triplet $[Os(NH_3)_5H]^{3+}$. In methanol there are two bending modes which are combinations of the (C)OH bend and the methyl rocking modes. These were computed to be 1330 and 1056 cm^{-1} for free methanol (with intensities 10.6 and 12.0 km mol^{-1}, respectively) and 1349 and 1077 cm^{-1} for bound methanol (with intensities 28.9 and 17.7 km mol^{-1}). Replacing the oxygen-bound hydrogen by deuterium yields 1214 and 873 cm^{-1} for bound CH_3OD (with intensities 7.1 and 44.7 km mol^{-1}). The analogous peaks in free CH_3OD were computed to be 1232 and 835 cm^{-1} (with intensities 0.3 and 44.8 km mol^{-1}). Thus, for $[Os(NH_3)_5H(CH_3OH)]^{3+}$ and its deuterated isotopomer, the computed frequencies of 1349 and 873 cm^{-1} correlate reasonably well with the observed frequencies of 1358 and 966 cm^{-1}, respectively. The level of agreement between theory and experiment is considered acceptable, given the known shortcomings of the theoretical model used and the neglect of solid-state effects in the calculations. Although the ratio of the computed frequencies is $1349/873 = 2.39^{1/2}$, this no longer represents an isotopic ratio for a particular single mode, but one involving two different modes. It is worth noting that, while in $[Os(NH_3)_5H(CH_3OH)]^{3+}$ the higher frequency OH bend is computed to be the more intense one, the situation is reversed on deuteration, with the low-frequency peak (at 873 cm^{-1}) becoming about 6 times more intense than its high-frequency partner. This behavior is consistent with the experimental findings of Li, Yeh, and Taube.[1] The effect of deuteration on the computed intensities is even more pronounced for free methanol, where on deuteration the ratio of the computed low- to high-frequency intensities changes from ∼1 to ∼150.

Population Analysis and Bonding

The electron densities of the complexes studied were analyzed by the Roby−Davidson (RD) method,[10,11] as implemented by Ahlrichs and co-workers.[12,13] The salient features of the analyses are summarized in Table 5. According to this analysis, the charge on Os ranges from ∼0.8 to 1.1 e when L_1 and L_2 are neutral (H_2O, CH_3CN), with somewhat larger fluctuations shown in the case of anionic ligands. The charge on the (protonic) hydrogen ligand is largely neutral, ranging from −0.13 to 0.21 e. The negative values occur only for L_1 and $L_2 = CN^-$, while the largest positive values are observed for L_1 and $L_2 = CH_3CN$. Thus, effectively the Os−H bond is between neutral hydrogen and Os(III), although the formal charge on Os is only ∼1 e. All the other ligands, therefore, carry a net positive charge or are less negative, in the case of anions, than the free ligands.

A shared electron number in the RD analysis is a measure of the degree of covalent bonding between two atoms. Clearly, in the case of the metal−hydrogen interaction, a strong covalent bond is indicated, consistent with a bonding interaction between two open-shell species with comparable open-shell MO energies. By contrast, the shared electron numbers between Os and the more conventional electron-pair-donating ligands are very much smaller, e.g., as low as 0.05 e when L_1 and $L_2 = H_2O$, although in the case of cyanide the shared electron numbers (that include σ donation and π back-bonding) are comparable with the values observed for Os−H. These findings are similar to those noted for a number of Pt(IV) complexes, where formally H^- as well as $CH_3{}^-$ were among the ligands.[35] For both of these ligands, the bonding to Pt was deduced to be covalent.

Conclusion

The $[Os(NH_3)_4H(L_1{}^{x})_m(L_2{}^{y})_n]^{(mx+ny+3)+}$ complexes (L_1 and $L_2 = H_2O$, NH_3, CH_3OH, CH_3CN, Cl^-, and CN^-) studied in this work could be regarded either as protonated Os(II) species or as hydrides of Os(IV), although our finding is that, in analogy with Pt−H bonds, the osmium−hydrogen interaction in these systems is best described as a covalent Os(III)−H bond. In general, the ground states are found to be singlets, with low-lying triplet excited states, with the triplet−singlet separation increasing on solvation. While spin−orbit coupling is expected to preferentially stabilize the triplets, the computed values in this work are not large enough to radically change the above conclusions. It is satisfying that the geometries and the electronic structures of the complexes can be interpreted and readily understood in terms of a simple Pauling-type hybridization model in conjunction with conventional ligand field theory. Such an approach provides a simple explanation for the observation that no true seven-coordinate triplet state complexes were found.

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(35) Mylvaganam, K.; Bacskay, G. B.; Hush, N. S. *J. Am. Chem. Soc.* **2000**, *122*, 2041.

Table 5. Roby−Davidson Analysis: Charges (q) on Selected Atoms/Ligands (in e) and Shared Electron Numbers (σ) between Selected Atoms Calculated from DFT(B3P86) Densities

complex[a]	q(H)	q(Os)	q(L)	q(L′)	σ(Os−H)	σ(Os−N)	σ(Os−X1)[b]	σ(Os−X2)[b]
$[Z\text{-}(H_2O)]^{3+}$ (singlet)	0.15	1.11	0.12		1.01	0.36	0.11	
$[Z\text{-}(H_2O)]^{3+}$ (triplet)	0.10	1.11	0.10		1.02	0.41	0.05	
$[Z\text{-}(H_2O)_2]^{3+}$ (cis, singlet)	0.13	1.10	0.09	0.14	0.96	0.34	0.10	0.10
$[Z\text{-}(H_2O)_2]^{3+}$ (cis, triplet)	0.04	1.09	−0.22	0.34	1.00	0.42	0.05	0.00
$[Z\text{-}(H_2O)_2]^{3+}$ (trans, singlet)	0.12	1.11	0.12	0.21	0.92	0.28	0.21	0.30
$[Z\text{-}(H_2O)_2]^{3+}$ (trans, triplet)	0.08	1.07	0.05	0.16	1.02	0.40	0.05	0.01
$[Z\text{-}(NH_3)]^{3+}$ (singlet)	0.11	1.09	0.35		0.94	0.34	0.39	
$[Z\text{-}(NH_3)]^{3+}$ (triplet)	0.07	1.26	0.10		1.00	0.36	0.08	
$[Z\text{-}(NH_3)(CH_3OH)]^{3+}$ (singlet)	0.17	0.94	0.23	0.20	1.04	0.31	0.22	0.19
$[Z\text{-}(NH_3)(CH_3OH)]^{3+}$ (triplet)	0.08	1.14	0.04	−0.02	1.00	0.38	0.07	0.01
$[Z\text{-}CN]^{2+}$ (singlet)	0.10	0.94	−0.19		0.99	0.21	1.19	
$[Z\text{-}CN]^{2+}$ (triplet)	−0.05	1.18	−0.20		0.92	0.22	1.11	
$[Z\text{-}(CN)_2]^{+}$ (singlet)	−0.13	0.94	−0.46	−0.41	0.56	0.10	0.81	0.80
$[Z\text{-}(CN)_2]^{+}$ (triplet)	0.10	1.34	0.20	0.14	0.76	0.15	0.97	0.51
$[Z\text{-}Cl]^{2+}$ (singlet)	0.15	0.72	−0.33		0.98	0.39	0.23	
$[Z\text{-}Cl]^{2+}$ (triplet)	0.10	1.00	−0.07		1.03	0.21	0.47	
$[Z\text{-}(Cl)_2]^{+}$ (singlet)	0.01	0.67	−0.60	−0.52	0.81	0.37	0.22	0.21
$[Z\text{-}(Cl)_2]^{+}$ (triplet)	0.03	0.93	−0.48	−0.59	0.98	0.35	0.32	0.11
$[Z\text{-}(CH_3CN)]^{3+}$ (singlet)	0.21	0.99	0.30		1.01	0.34	0.29	
$[Z\text{-}(CH_3CN)]^{3+}$ (triplet)	0.12	1.10	0.36		0.89	0.30	0.51	
$[Z\text{-}(CH_3CN)_2]^{3+}$ (singlet)	0.14	0.73	0.07	0.52	0.96	0.29	0.34	0.38
$[Z\text{-}(CH_3CN)_2]^{3+}$ (triplet)	0.00	1.05	0.02	0.32	0.96	0.44	0.43	0.13

[a] $Z = [Os(NH_3)_4H]$. [b] X1 and X2 are the ligand atoms which form bonds with Os.

However, the apparently seven-coordinate triplet-state complex $[Os(NH_3)_5H(CH_3OH)]^{3+}$, whose existence had been reported by Li, Yeh, and Taube,[1] is predicted to be a stable six-coordinate complex which is fairly strongly bound to a methanol molecule in the second coordination shell. However, according to the computations, the singlet and triplet states are, in effect, comparable in their stabilities. On the other hand, in the case of $[Os(NH_3)_4H(CH_3CN)_2]^{3+}$, the computations were not stable and hence do not provide clear predictions of electronic structure.

Acknowledgment. We are pleased to acknowledge helpful discussions with Professor Henry Taube (Stanford University). This work was supported by the Australian Research Council.

Supporting Information Available: Tables S1 and S2, listing gas-phase total energies, solvation energies, and zero-point energies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA003723R