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Near Doubling of H–H Bond Length in the "Stretched" Osmium Molecular Hydrogen Complex $[Os(NH_3)_4OAc(\eta^2\text{-}H_2)]^+$: A Theoretical Study

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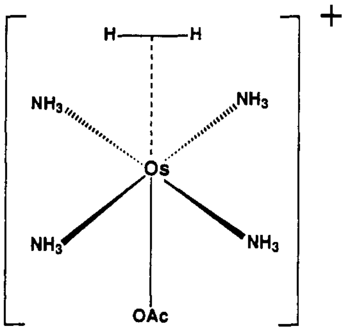
Dihydrogen complexes represent an important new area of transition metal chemistry. The first such complex was described by Kubas et al.[1] in 1984, but many more have since been synthesized. The nature of the H_2 binding and the overall electronic structures of these systems are naturally of great interest. In 1971 Malin and Taube[2] reported the preparation of the $[Os(en)_2H_2]^{2+}$ complex which was thought to be a *cis*-dihydride but is now recognized as a dihydrogen complex.[3] Li and Taube[3] also described the synthesis of an analogous series of d^6 complexes of general formula $[Os(NH_3)_4L^zH_2]^{(2+z)+}$ (**1**), where L^z is a ligand with charge *z*. These are described as η^2-H_2 complexes and display large variations in their physical (as determined by NMR) as well as chemical properties, with facile substitution of the ligand L^z. For $[Os(en)_2OAc(\eta^2\text{-}H_2)]^+$ (**2**) (in its PF_6^- salt) low temperature neutron diffraction measurements were also carried out, which indicate that H_2 is sideways bonded and lies between the N–Os–N axes.[4] The most remarkable feature of this ion is the very long H–H bond: 1.34 ± 0.02 Å, approximately twice as long as in free H_2 (0.741 Å). This is in marked contrast, for example, to the neutral W d^6 complex $[W(CO)_3(P^iPr_3)_2(\eta^2\text{-}H_2)]$ of Kubas (**3**), where low-temperature neutron diffraction confirms that H_2 is also sideways bonded, with the H_2 axis parallel to the P–W–P axis, but the H–H bond length is only 0.82 ± 0.01 Å.[5] In addition, it has been found that in toluene solution rapid interconversion between the complex **3** and a 7-coordinate dihydride occurs.[6] Self-consistent field (SCF) quantum chemical calculations confirm the existence of at least two stable isomers, predicting H–H distances of approximately 0.8 and 1.9 Å for the dihydrogen and *cis*-dihydride respectively.[7,8]

A stretched H–H distance (1.357 Å) has also been recently observed in the rhenium polyhydride $[ReH_7(P(C_6H_4CH_3\text{-}4)_3)_2]$ by neutron diffraction;[9] similar distances (1.24–1.43 Å) are inferred from ^1H NMR spin–lattice hydride relaxation time data when different triarylphosphines are used.[10] However, we believe that the title compound is the first stretched H_2 structure identified by neutron diffraction which is not, at least in part, the consequence of the crowded nature of a highly coordinated polyhydride complex.

We have carried out quantum chemical calculations on a number of species with the general formula **1**, in order to correlate their geometric characteristics with the experimental NMR and other physical data, including $[Os(NH_3)_4OAc(\eta^2\text{-}H_2)]^+$ (**2′**), where the OsH_2 fragment is expected to be very similar to that in **2**. As the latter is the only one for which structural information is as yet available, we confine discussion in this communication to **2′**. The calculations were performed using effective core potentials (ecp) in conjunction with valence basis sets.[11] The Os ecp include relativistic corrections. Geometry optimizations were carried out at the SCF level on (**2′**) assuming C_s symmetry, at a range of H–H and Os–H distances, resulting in a two dimensional representation of the potential energy surface. At each grid point (where all other bond lengths and angles had been optimized) the correlation energy of the complex was calculated, using second order Møller–Plesset (MP2) perturbation theory. Thus MP2 optimized values for the H–H and Os–H distances have been obtained with all other coordinates optimized at the SCF level. All calculations were performed with the HONDO suite of programs.[12]



2′

The results of the H–H bond length optimization are summarized in Figures 1 and 2, where the distance dependence of the SCF and MP2 energies of **2′** is shown and contrasted with that in free H_2. There are three important points to note. The first is that the SCF potential energy curve corresponding to **2′** is unusually flat, implying a very low H–H stretching force constant. In such a situation small perturbations, e.g. substitution of another ligand for OAc^-, as in the series **1**, may lead to disproportionately large changes in the physical and chemical properties, as indeed has been observed.[3] The second point is that there is only one cis isomer, i.e. no potential barrier separating a η^2-H_2 complex and a *cis*-dihydride. (Although no results are shown at H–H distances larger than 1.5 Å, calculations were carried out at separations out to 2.2 Å.) Third, given the shallow potential energy curve, the electron correlation effects are unusually important and result in a H–H distance of 1.39 Å, to be compared with the SCF value of 0.85 Å. The Os–H distance has been found to be much less sensitive to correlation, the MP2 and SCF values being 1.58 and 1.73 Å, respectively. In striking contrast to these results, the free H_2 potential energy curves are quite

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† Department of Physical and Theoretical Chemistry.

‡ Department of Biochemistry.

(1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984,** *106,* 451.

(2) Malin, J.; Taube, H. *Inorg. Chem.* **1971,** *10,* 2403.

(3) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991,** *113,* 8946.

(4) Hasegawa, T.; Koetzle, T. J.; Li, Z.; Parkin, S.; McMullan, R.; Taube, H. *29th International Conference on Coordination Chemistry;* Lausanne, Switzerland, 1992.

(5) Vergamini, P. J.; Wasserman, H. J.; Kubas, G. J.; Koetzle, T. J.; Ryan, R. R. Unpublished results quoted as ref 8 in: Eckert, J.; Kubas, G. J.; Hall, J. H.; Hay, P. J.; Boyle, C. M. *J. Am. Chem. Soc.* **1990,** *112,* 2324.

(6) Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van der Sluys, L. S.; Kubat-Martin, A. *J. Am. Chem. Soc.* **1990,** *112,* 3855.

(7) Craw, J. S.; Bacskay, G. B.; Hush, N. S. To be published.

(8) (a) Hay, P. J. *Chem. Phys. Lett.* **1984,** *103,* 466. (b) Hay, P. J. *J. Am. Chem. Soc.* **1987,** *109,* 705.

(9) Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991,** *4,* 241.

(10) Michos, D.; Lou, X.-L.; Howard, J. A. K.; Crabtree, R. H. *Inorg. Chem.* **1992,** *31,* 3914.

(11) Os: Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990,** *77,* 123. C, N, O: Igel-Mann, G.; Stroll, H.; Preuss, H. *Mol. Phys.* **1988,** *65,* 1321. H (plus p functions (ζ_p = 0.8) on the η^2-H_2): Huzinaga, S. *J. Chem. Phys.* **1965,** *42,* 1293.

(12) Dupuis, M.; Rys, J.; King, H. F. *J. Chem. Phys.* **1976,** *65,* 111.

0020-1669/93/1332-2230$04.00/0

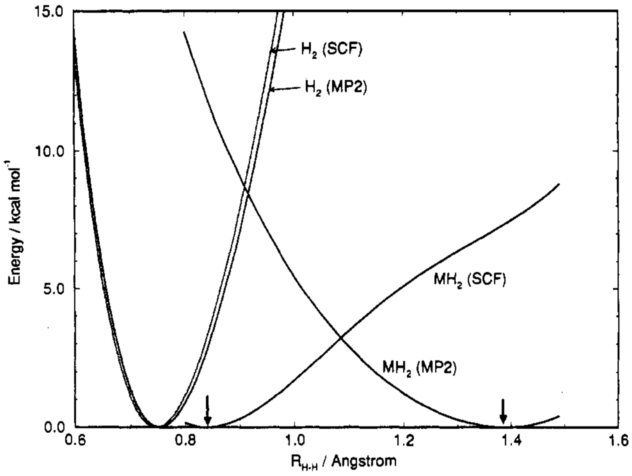


Figure 1. SCF and MP2 energies for molecular hydrogen and the dihydrogen complex $[Os(NH_3)_4OAc(\eta^2\text{-}H_2)]^+$ as a function of the H–H bond length ($M \equiv [Os(NH_3)_4OAc]^+$). The MH_2 minima are indicated by arrows.

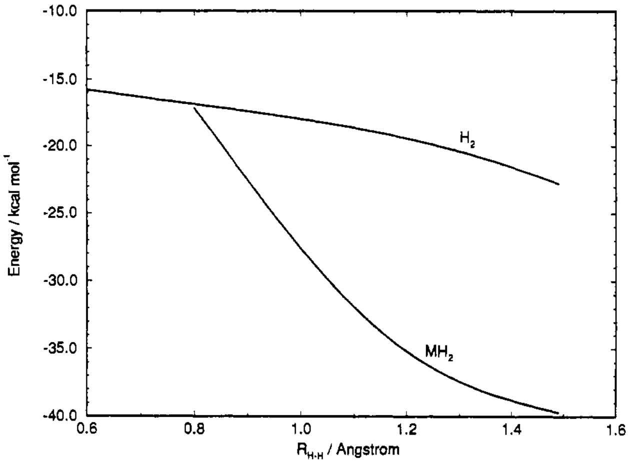
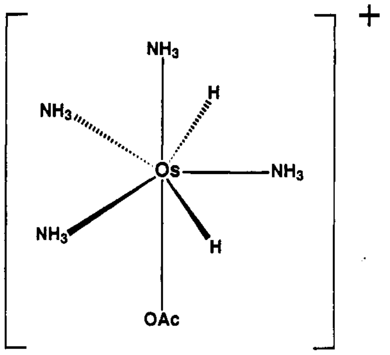


Figure 2. MP2 correlation energy ($E^{(2)}$) for molecular hydrogen and the dihydrogen complex $[Os(NH_3)_4OAc(\eta^2\text{-}H_2)]^+$ as a function of the H–H bond length ($M \equiv [Os(NH_3)_4OAc]^+$). Actual value plotted for MH_2 is $E^{(2)} + 665.8$ kcal mol^{-1}.

different, inasmuch as the SCF and MP2 curves are qualitatively the same and give rise to a high force constant. Furthermore, the MP2 correlation energy of the complex decreases significantly faster in the critical region of 0.8–1.4 Å than that of free H_2; hence the large correlation effect in **2′**. At this point we note that more extensive calculations[7] on $[Os(NH_3)_4Cl(\eta^2\text{-}H_2)]^+$ using MP3 and the averaged coupled pair functional (ACPF) technique[13] have yielded H–H distances in close agreement with the MP2 prediction, leading strong support to the reliability of the results in this paper.

The MP2 H–H and Os–H bond lengths in **2′**, viz. 1.39 and 1.58 Å respectively, are in acceptable agreement with the corresponding experimental values for **2**: 1.34 ± 0.02 and 1.60 ± 0.01 Å. The remaining bond lengths and angles, where comparisons are appropriate, are also in reasonable agreement with the observed values.[4] The absence of a stable *cis*-dihydride and the very low H_2 force constant point to further similarities between **2** and **2′**. SCF calculations on a dihydrogen complex of Os^{2+} with the same ligands as in the W complex (CO, PH_3) also resulted in a single stable η^2-H_2 complex, i.e. no *cis*-dihydride was found. It appears therefore that the formation of such a dihydride in the systems considered is governed principally by the electronic structure of the metal rather than of the ligands.

Other 7-coordinate distal dihydrides were identified, where the hydrogens are separated by one of the other ligands, but they lie relatively high in energy above the η^2-H_2 minimum. An example is **4**, which lies ca. 26 kcal/mol above **2′**.



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A major finding of this study is the inability of the SCF method to reliably predict the geometry of **2′**, and possibly other stretched H_2 complexes. The results of our calculations on a series of Os^{2+} and W dihydrogen complexes, including analyses of the bonding mechanisms, will be published shortly.

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(13) Gdanitz, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1988**, *143*, 413.