or ionic bonding. This allows all spin couplings (different VB structures), a particular important effect for atoms with partially filled d configurations. For wave functions with N VB pairs, this leads to $3^N$ configurations and hence three configurations for (1/2) and 81 configurations for (4/8). These calculations are dissociation-consistent: GVB-RCI(1/2) dissociates to a Hartree-Fock (HF) description of both M$^+$ and CH$_3$; GVB-RCI(4/8) dissociates to an HF description of M$^+$ and a GVB-RCI(3/6) description of CH$_3$. For the metal hydrides the GVB-RCI(1/2) calculations dissociate to HF fragments.

(3) RCI(1/2)$\times$D$_2$. From the three RCI configurations all single and double excitations are allowed out of the metal-ligand $\sigma$ bond to all virtual orbitals. This calculation allows for all correlation between the two electrons of the bond pair. It dissociates to an HF$\times$S$_{val}$ description for both the metal ion and the CH$_3$ fragments (the single excitation is from the $s$ or $d_z$ orbital on the metal, depending on which is used for bonding, and from the $p_z$ orbital on CH$_3$). Metal hydrides dissociate to an HF$\times$S$_{val}$ description of M$^+$ and an HF H atom.

(4) RCI(1/2)$\times$(D$_2 + S_{non}$). To the configurations of (3) we add all those formed by starting with the RCI configurations and allowing single excitations from the metal nonbonding valence orbitals (to all occupied and virtual orbitals). This calculation dissociates to an HF calculation on the ligand and an all singles CI for the metal valence orbitals.

(5) RCI(1/2)$\times$(D$_2 + S_{non, val}$). This calculation is similar to (4) except that the single excitations are allowed out of all valence orbitals, not just those of the metal ion. For the metal hydrides the two calculations are the same. The metal methyls dissociate to an HF$\times$S$_{val}$ description on both fragments. This leads to an overcorrelation of the fragments in some cases (if single excitations on the metal lead to an energy lowering, e.g., ZnCH$_3^+$, PdCH$_3^+$, and CdCH$_3^+$) and hence to calculated dissociation energies that may be slightly too low. This effect is not large and calculations by Carter and Goddard$^{22}$ on RuCH$_3$ involving a similar dissociation error show that the bond energy is underestimated by $\sim$0.2 kcal/mol. We expect a similar error in our cases. As a test of the adequacy of this level of electron correlation, Carter and Goddard$^{26}$ performed a similar calculation breaking the C–H bond in CH$_4$. The theoretical bond dissociation energy was calculated at 110.5 kcal/mol in comparison to an experimental $D_e$ of 112.2 $\pm$ 0.5 kcal/mol. The calculated bond dissociation energy is thus only 1.7 kcal/mol lower than the experimental value, suggesting that our comparable calculations on MCH$_3^+$ species should be quite adequate.

Acknowledgment. We thank the National Science Foundation (Grants CHE83-18041 and CHE84-07857) for partial support of this work.

Bond Energy and Other Properties of the Re–Re Quadruple Bond

David C. Smith and William A. Goddard III*

Contribution No. 7558 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. Received February 18, 1987

Abstract: Using generalized valence bond (GVB) methods designed for obtaining accurate bond energies, we predict an Re–Re quadruple bond strength of 85 $\pm$ 5 kcal/mol for Re$_2$Cl$_8^2$ $^\circ$. This is much less than early estimates of 370 kcal/mol found in thermochemical study (97 $\pm$ 12 kcal/mol). We obtain a rotational barrier of 3.0 kcal/mol and a singlet-triplet excitation energy of 3100 cm$^{-1}$, and we conclude that the intrinsic strength of the $\delta$ bond is $6 \pm 3$ kcal/mol.

Since their discovery in 1965, quadruply bonded metal dimers have provoked numerous theoretical and experimental studies. A particularly controversial issue has been the strength of the quadruple bond and, in particular, the contribution of the $\delta$ bond to the observed structure of the unbridged dimers.$^{1,4}$ We here report the results of ab initio calculations of Re$_2$Cl$_8^2$ designed to provide accurate bond energies and torsion barriers as well as accurate shapes for the potential curves. These studies use the generalized valence bond (GVB) approach in which electron correlations are included for all eight electrons available for the quadruple bond, while solving self-consistently for all orbitals.$^{5,6}$

We use the modified-GVB (M–GVB) approach of Goodgame and Goddard.$^1$ They pointed out that ab initio descriptions of multiple bonds in transition to a calculated dissociation energy that the bond energy due to an inadequate treatment of the electron correlations in the ion pair of the wave function describing the bond.

$$\Psi_{\text{GVB}} = \psi_{\text{cor}} + \lambda \psi_{\text{ionic}} = [\phi_1(1)\phi_2(2) + \phi_1(1)\phi_2(2)] + \lambda[\phi_1(1)]\phi_2(2) + [\phi_1(1)\phi_2(2)]$$

In GVB, electron correlation in the covalent part of the wave function.
Bond Energy of the Re–Re Quadruple Bond

Figure 1. GVB orbitals involved in the σ, π, and δ bonds of Re₂Cl₈²⁻ (reading top to bottom). Spacing between contours is 0.05 au. Negative contours are denoted by dashed lines; asterisks denote position of nuclei. The σ and π orbitals are plotted in the xy plane; the δ orbitals are plotted in a plane rotated 45° from the xy plane.

Figure 2. Energy profile for the ground state and 3(δ*) excited state of Re₂Cl₈²⁻ as a function of dihedral angle. The 3(δ* → σ*) excitation energy was calculated for δ = 0° and 45°. The plot assumes a periodic energy function with the energies at δ = 6° of 0° and 45° as the minimum and maximum of the function for the ground state and the maximum and minimum of the function for the 3(δ*) excited state.

Figure 3. Calculated potential curves for Re₂Cl₈²⁻.

Table I. Comparison of Calculated and Experimental Spectroscopic Constants

<table>
<thead>
<tr>
<th></th>
<th>GVB-PP ¹</th>
<th>GVB-RCI b</th>
<th>M-GVB-RCI</th>
<th>expl</th>
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<tbody>
<tr>
<td>bond length (Å)</td>
<td>2.37</td>
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<td>2.36</td>
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<td>Re-Re force constant (mdyn/Å)</td>
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<td>240</td>
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<tr>
<td>bond energy (kcal/mol)</td>
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<td>97 = 12</td>
</tr>
<tr>
<td>rotational barrier (kcal/mol)</td>
<td>-1.6</td>
<td>0.1</td>
<td>2.8</td>
<td></td>
</tr>
</tbody>
</table>

¹For a description of GVB-PP wave functions, see ref 6. ²CI wave function similar to that described in Table 1a of M. B. J.; Goodchild, W. A., III J. Chem. Phys. 1975, 63, 3523-3531. ³Based on X-ray diffraction study of K₃[Re₂Cl₈]·2H₂O: ref 9. ⁴The calculated Re–Re bond length and force constants were used with an earlier determined valence force field in the vibrational analysis: ref 22. ⁵Based on solid-state resonance Raman study of (n-Bu₄N)₄[Re₂Cl₈]: ref 24. ⁶Based on thermochemical study of Cs₂Re₂Br₈: ref 14. ⁷Keeping a constant spin coupling, GVB-PP leads to a dissociation error of 55.5 kcal/mol.

In crystals and solution, the charge of Re₂Cl₈²⁻ is potentials (ECP) so that only the 15 outermost electrons (5s,5p,6s,5d) of each Re are treated explicitly; however, the potentials describe the effects of core electrons including the dominant relativistic effects.

The GVB orbitals of the singlet ground state (1A₁g) are shown in Figure 1 where we see that four electrons in dx, dxz, dyz, and dxy orbitals on each Re are spin-paired to form the quadruple bond. Uncoupling the spins of the two electrons in δ orbitals leads to the lowest triplet state (3A₂g). Rotating one ReCl₅ group about the bond by 45° leads (see Figure 2) to essentially identical bonding in the π, σ, π, and δ orbitals, but the δ bond is broken with the result that the singlet and triplet states (denoted as 1B₁ and 1A₂) are nearly degenerate. Some indications of the relative strengths of these bonds are given by the overlaps in the GVB orbitals. S₅ = 0.68, S₆ = 0.54, S₇ = 0.12 for the eclipsed configurations, but S₅ = 0.68, S₆ = 0.53, and S₇ = 0.0 for the staggered. As the bond is stretched, the overlaps of the GVB orbitals decrease continuously to zero, leading to a smooth description of bond dissociation (molecular orbital based schemes often lead to the wrong dissociation limit, complicating predictions of bond energies).

In these calculations the geometry of each (Re₂Cl₈)²⁻ fragment was fixed as that in the crystal, and the Re–Re bond distance was optimized. An important issue here for bond energies concerns the charges. In crystals and solution, the charge of Re₂Cl₈²⁻ is

neutralized by counter charges (e.g., K\(^+\)), and in calculating bond energies, it is necessary to include the effects of these counter charges (the Coulomb energy for two charges at 2.24 Å is 150 kcal/mol). In order to ameliorate this problem, fractional charges (leading to a net charge of 0 on each fragment) are placed at positions extrapolated from the crystallographic positions of the counterions. The charges are placed so as to maintain the overall symmetry of the system and to be invariant under a 45° rotation of the ReCl\(_4\) units. The rotational invariance allows for a comparison of the properties of the eclipsed and staggered geometries. The results for the Re–Re bond distance optimization are shown in Figure 3 and in Tables I and II.\(^{11}\)

The bond energy for the Re–Re quadruple bond calculated at the M–GVB level is 85.0 kcal/mol, the first ab initio estimate of the energy of a quadruple metal–metal bond. Similar calculations on Mo\(_2\) and Cr\(_2\) lead to bond energies within 5 kcal/mol of experiment, and we believe that similar accuracy can be expected in the Re–Re quadruple bond studies, leading to \(D_2\) (Re–Re) = 85 ± 5 kcal/mol. A more conservative estimate of the uncertainty, perhaps ±10 kcal/mol, would be warranted given the lack of comparable theoretical and experimental studies on other systems. Experimental values for the bond energy of the quadruple bond have been quite difficult to obtain. Early estimates have ranged as high as 370 kcal/mol. Birge–Sponer extrapolations using the harmonic stretching frequency and the anharmonicity constant determined from resonance Raman measurements suggest an Re–Re bond energy of 152 ± 19 kcal/mol for ReCl\(_4\)\(^2\) and 139 ± 24 kcal/mol for ReBr\(_4\)\(^2\). Such Birge–Sponer extrapolations for multiple bonds are fraught with peril and could easily lead to errors of 50–70 kcal/mol.\(^{13}\) A more reliable thermochemical study places the Re–Re bond energy for C\(_5\)Re\(_2\)Br\(_7\) at 97 ± 12 kcal/mol,\(^{14}\) this estimate depending on empirically based assumptions in order to estimate the Re–Br bond energy. Given the various experimental uncertainties, we believe that the theoretical value of 85 kcal/mol is the best current estimate of the bond energy. Early extended Hückel calculations placed the quadruple bond in ReCl\(_4\)\(^2\) at 370 kcal/mol. Recent theoretical work with the Hartree–Fock–Slater transition-state method has estimated the Re–Re triple bond energy in ReCl\(_4\)(PH\(_3\))\(_4\) to be 134 kcal/mol.\(^{15}\) Generally, these latter methods lead to an overestimate of the bond energy by 1 to 2 eV,\(^{16}\) suggesting \(D_2\) ~ 90 to 110 kcal/mol, in line with the GVB results.

<table>
<thead>
<tr>
<th>(\text{ReCl}_4) (\text{ReBr}_4)</th>
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<td>293</td>
<td>293</td>
</tr>
<tr>
<td>bond energy (kcal/mol)</td>
<td>85.0</td>
<td>76.5</td>
</tr>
</tbody>
</table>

*Optimization of eclipsed rotomer neglecting relaxation of ReCl\(_4\) fragments from their ground-state structure.*

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(10) An average metal–ion distance of 4.3 Å was maintained (determined from the X-ray diffraction data). Charges of +0.125 were placed in the same positions extrapolated from the crystallographic positions of the counterions. The charges are placed so as to maintain the overall symmetry of the system and to be invariant under a 45° rotation of the ReCl\(_4\) units.\(^{10}\) The rotational invariance allows for a comparison of the properties of the eclipsed and staggered geometries. The results for the Re–Re bond distance optimization are shown in Figure 3 and in Tables I and II.\(^{11}\)

The bond energy for the Re–Re quadruple bond calculated at the M–GVB level is 85.0 kcal/mol, the first ab initio estimate of the energy of a quadruple metal–metal bond. Similar calculations on Mo\(_2\) and Cr\(_2\) lead to bond energies within 5 kcal/mol of experiment, and we believe that similar accuracy can be expected in the Re–Re quadruple bond studies, leading to \(D_2\) (Re–Re) = 85 ± 5 kcal/mol. A more conservative estimate of the uncertainty, perhaps ±10 kcal/mol, would be warranted given the lack of comparable theoretical and experimental studies on other systems. Experimental values for the bond energy of the quadruple bond have been quite difficult to obtain. Early estimates have ranged as high as 370 kcal/mol. Birge–Sponer extrapolations using the harmonic stretching frequency and the anharmonicity constant determined from resonance Raman measurements suggest an Re–Re bond energy of 152 ± 19 kcal/mol for ReCl\(_4\)\(^2\) and 139 ± 24 kcal/mol for ReBr\(_4\)\(^2\). Such Birge–Sponer extrapolations for multiple bonds are fraught with peril and could easily lead to errors of 50–70 kcal/mol.\(^{13}\) A more reliable thermochemical study places the Re–Re bond energy for C\(_5\)Re\(_2\)Br\(_7\) at 97 ± 12 kcal/mol,\(^{14}\) this estimate depending on empirically based assumptions in order to estimate the Re–Br bond energy. Given the various experimental uncertainties, we believe that the theoretical value of 85 kcal/mol is the best current estimate of the bond energy. Early extended Hückel calculations placed the quadruple bond in ReCl\(_4\)\(^2\) at 370 kcal/mol. Recent theoretical work with the Hartree–Fock–Slater transition-state method has estimated the Re–Re triple bond energy in ReCl\(_4\)(PH\(_3\))\(_4\) to be 134 kcal/mol.\(^{15}\) Generally, these latter methods lead to an overestimate of the bond energy by 1 to 2 eV,\(^{16}\) suggesting \(D_2\) ~ 90 to 110 kcal/mol, in line with the GVB results.
Ligand-Aided Photoreduction of Iron–Porphyрин Complexes Probed by Resonance Raman Spectroscopy

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Abstract: Photoreduction has been observed for the first time for an iron porphyrin with a biologically relevant axial ligand by using resonance Raman (RR) spectroscopy (for FeIII(OEP)(2-MeIm). OEP = octaethylporphyrin and 2-MeIm = 2-methylimidazole). The action spectrum for the photoreduction obtained by visible absorption spectra exhibited a broad maximum around 420–460 nm, which was appreciably shifted from the Soret band of FeIII(OEP)(2-MeIm) at 395 nm. Similar photoreduction was observed for FeIII(OEP)(1,2-Me2Im) (1,2-Me2Im = 1,2-dimethylimidazole) but not for FeIII(OEP)L2 (L = imidazole and 1-methylimidazole) and FeIII(OEP)X (X = F, Cl, Br, I, and ClO4). The coincidence of the RR spectrum of the photoreduced species with that of the ferrous porphyrin rules out the possibility of ring reduction to a porphin anion radical or chlorin. The dependence of the photoreduction on the concentration of 2-MeIm suggested that the ligand-free FeIII(OEP) is a likely intermediate and thus that the light-induced charge transfer from the axial ligand to the iron ion is the primary process of photoreduction.

In the resonance Raman (RR) studies of some heme proteins, occurrence of photoreduction has been noticed upon laser irradiation at selected wavelengths, but nothing is known about its mechanism and electron donors. Apart from these studies, the photoreduction has been explored for several metalloporphyrins from the view of photochemistry, although no Raman study has been included. To gain an insight into the photoreduction mechanism of hemeproteins, we investigated iron porphyrin complexes with a biologically relevant axial ligand by using RR spectroscopy. The use of this technique might allow us to infer an intermediate molecular species involved in the photoreduction on the basis of the accumulated knowledge about the RR spectra of iron porphyrins.

Here we report RR evidence for photoreduction of 2-methylimidazole (2-MeIm) and 1,2-dimethylimidazole (1,2-Me2Im) complexes of iron-octaethylporphyrin [FeIII(OEP)] and point out the formation of the four-coordinate ferrous complex as an intermediate.

**Experimental Procedures**

FeIII(OEP)X (X = F, Cl, Br, I, and ClO4) were synthesized with the methods described elsewhere. 2-MeIm was recrystallized just before use, and its 1H NMR spectrum showed that it did not contain any detectable impurity. The procedures for preparing the alkyl-imidazole complexes of FeII(OEP)X and FeII(OEP)(2-MeIm) were described previously. As a solvent dichloromethane (CH2Cl2) of spectroscopic grade (Wako, Osaka) was used without further purification. All solutions were degassed unless otherwise stated and kept at 0°C during the Raman measurements.

Raman spectra were measured with a JOEL-400D Raman spectrometer equipped with a RCA-31034a photomultiplier. The excitation sources used are Kr+ (Spectra Physics, Model 164), He/Cl (Kinmon Electrics, Model CDR80MG), and Ar+ (NEC, Model GLG3200) lasers. Raman shifts were calibrated with indene, and errors of peak frequencies would be less than 1 cm⁻¹ for well defined bands. Conventional absorption spectra were recorded with a Hitachi 1245 spectrophotometer.

**Acknowledgment.** We acknowledge Dr. Siddharth Dasgupta for his contributions in the vibrational analysis. This work was partially supported by grants from the Sun Co. and from National Science Foundation (No. CHE83-18041).