Nuclear Motion in the σ-Bound Regime of Metal–H₂ Complexes: [Mg(H₂)_{n=1–6}]^{2+}

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Supporting Information

ABSTRACT: The dynamic, quantum structure of [Mg(H₂)_{n=1–6}]^{2+} complexes is investigated via ab initio path integral molecular dynamics simulations. These complexes represent the strong, σ-complex regime of metal–H₂ interactions and are representative of bonding motifs found in metal–organic frameworks. Significant nuclear motion within the coordination sphere is observed, even though the ligands remain largely intact. Quantum effects are found to be important in the H–H and metal–H₂ stretch coordinates, but the remaining motion in the molecule is well represented by classical simulations. Nearly free rotation of the dihydrogen moiety is observed in all complexes. Statistical averages and distributions of structural parameters are found to deviate nontrivially from the same parameters in static, equilibrium structures.

INTRODUCTION

The prediction and discovery of nonclassical dihydrogen ligands (so-called σ complexes) in the early 1980s once again challenged a chemist’s definition of a chemical bond. Rather than a canonical H–M–H dihydride bonding configuration, σ-H₂ complexes exhibit an η¹ bonding interaction between a metal center and the σ bond density of the nominally H₂ moiety. In the decades following these reports, numerous additional examples of M–H₂ complexes were discovered, including complexes with characteristics intermediate to the dihydride and σ complex regimes.

Owing to this nonclassical three-center, two-electron bonding motif, theoretical and experimental studies have frequently addressed the electronic factors governing the ligand’s configuration. Electrostatics, as well as forward donation from the σ bond of the H₂ ligand to a p orbital of the metal center, provide a significant fraction of the driving force for the roughly 15–20 kcal/mol of complexation energy. Back-donation effects from an occupied d orbital of the metal to the empty σ* orbital of the H₂ also dictate the position of the complex on the sliding scale between dihydride and σ-complex configurations. Additional contributions from trans-ligand and cis-hydride effects provide further synthetic flexibility in generating complexes with desired properties.

This ability to tailor the binding strength and configuration of the H₂ unit has led to the use of dihydride/dihydrogen complexes in an enormous variety of chemistry. The hydride form has long been utilized in catalytic hydrogenation, which is “perhaps the most important catalytic method in synthetic organic chemistry”. Industrial applications often use a heterogeneous version of this process, whereas many synthetic reactions, including recent successes in asymmetric catalysis, employ homogeneous catalysts. At the other end of this family of binding configurations, σ-complex interactions have been shown to be useful in metal–organic framework materials for hydrogen storage applications. The competing effects of forward- and back-donation, along with ligand effects, have been used to tailor the binding energy of such storage systems.

This report addresses nuclear motion in σ-H₂ complexes, including the degree to which a static structure is viable and the manner in which zero-point energy and thermal motions modify the static picture. Inelastic neutron scattering experiments have used the inherent motion (or lack thereof) in such complexes to infer the barrier heights to H₂ rotation. In fact, this nuclear motion was a key piece of evidence in the quantification of forward- and back-donation effects. The forward donation is isotropic along the axis perpendicular to the H₂ bond, so any extant barrier is indicative of back-donation. Such a one-dimensional picture, however, is severely limited and ignores the additional zero-point and thermal motion in the remainder of the molecule, which will be shown to be significant in this work. Nuclear motion in dihydride and intermediate complexes remains an open question and will be the focus of future studies, but this work analyzes the σ-complex limit of this family of compounds. In particular, nuclear motion in the series of [Mg(H₂)_{n=1–6}]^{2+} complexes has been analyzed via ab initio path integral simulation techniques. These compounds have been chosen because they fall squarely in the σ-complex regime. The divalent magnesium cation...
provides a strong interaction with the H₂ σ bond, whereas the lack of d orbital occupation prevents back-donation effects. Magnesium metal sites for hydrogen interaction are also of interest in metal–organic frameworks. Key questions to be addressed include the fluxional nature of the structure of this complex, as well as the role of quantum mechanical zero-point motion in determining such properties.

**METHODS**

Computational assessment of structural flexibility in metal–H₂ complexes requires an accurate treatment of the electronic structure (which dictates the propensity and directionality of bonding) as well as an accurate description of the quantum mechanical nuclear motion. Ab initio path integral methodology provides a route to tackling both halves of this problem. Path integral methods map a quantum particle onto harmonically coupled, classical replicas of the system, colloquially referred to as a “ring polymer”, and generate a potentially exact representation of the quantum, thermal motion. The spread and movement of the ring polymer account for quantum delocalization. Sampling via now-standard Monte Carlo (PIMC) or molecular dynamics (PIMD) algorithms provides an efficient route for computing the nonlocal excursions through configuration space. When coupled with an electronic structure theory-based underlying potential energy surface, ab initio path integrals generate a first-principles and systematically improvable approach to a fully quantum mechanical simulation of the system.

In this work, second-order Møller–Plesset perturbation theory (RI-MP2) was used as the underlying potential method. As shown in Table S1 of the Supporting Information, the RI-MP2 method is consistent with coupled-cluster theory [CCSD and CCSD(T)] benchmarks for the binding energy of the H₂ unit, structural parameters at equilibrium, and harmonic H₂ stretch frequencies in the limiting cases of [Mg(H₂)]²⁺ and [Mg(H₂)₆]²⁺. The benchmarking results demonstrate that the qualitative structure is consistent across all polarization function-containing basis sets. The cc-pVDZ basis set was chosen in this work as a reasonable compromise of accuracy and the computational efficiency required for configurational sampling. While the high-frequency H−H harmonic stretch in [Mg(H₂)]²⁺ is overestimated in this method by 102 cm⁻¹, the relative shift in frequency between bare H₂ and the metal complex is well reproduced by RI-MP2/cc-pVDZ (423 cm⁻¹) compared to large basis set CCSD benchmarks (433 cm⁻¹). Lower-frequency motions, such as the embedded H₂ rotor motions, are moderately sensitive to the level of theory, but given the extremely low barriers to this motion (see below), the resulting structural distributions are not particularly sensitive to this quantity.

The nuclear motion was simulated via the aforementioned PIMD method at 300 K, and analogous classical simulations were performed for comparison. The ring polymer consisted of 32 system replicas in the PIMD simulations, which is sufficiently converged for H-containing systems within the second-order Trotter expansion. A multiple-time-step algorithm for analytically propagating the ring polymer normal modes was employed within a velocity Verlet integrator, using a conservative time step of 0.25 fs and a stochastic Langevin thermostat with a time constant of 1 ps for the centroid motion. The PIMD results were sampled via 20 independent simulations of 100 000 steps (25 ps) each, except for the [Mg(H₂)]⁶²⁺ complex, which was sampled with only 50 000 steps (12.5 ps) for each trajectory. Analogous classical MD simulations (1 system replica) were performed using the same integration time step, thermostat parameter, and trajectory length. This level of sampling was sufficient to reliably resolve the subtle structural changes that occur in these complexes. All MD and PIMD calculations were performed in an MPI-based, parallel version of the Q-Chem 4.2 quantum chemistry software package. Analysis of statistical averages, distributions, and errors was performed via in-house routines using the Q-Chem results. Statistical errors in computed averages were determined via a blocking analysis. Molecular structures were generated with the VMD software package.

**RESULTS AND DISCUSSION**

Static and statistical structural information is presented in the following section. Since the static structures of these complexes have been reported previously, emphasis is placed on the structural trends and the manner in which a dynamic picture modifies the static structure.

**Static Structure and Trends.** The optimized equilibrium structures of the [Mg(H₂)₃n₋₁₋₄]²⁺ complexes are shown in Figure 1 and are consistent with structures reported in previous studies. All of the hydrogen units bind in an η² fashion, and the first coordination sphere of the Mg²⁺ ion is completed at n = 6 with an octahedral configuration. No appreciable attraction between the ligands is observed, as all complexes adopt configurations that maximize distance between neighboring ligands. The lone exception to this maximization is complex 5, which exhibits a trigonal bipyramidal structure. In all cases, slight twisting of the dihydrogen ligands minimizes the subtle electronic repulsions between them.

Consistent with the energetic trends computed in the benchmark results (Table S1 in Supporting Information), the H−H bond lengths indicate that the influence of the ion is distributed across the H₂ units and, therefore, diminishes on a per-H₂ basis as the complex size increases. The single H₂ ligand in [Mg(H₂)]²⁺ is moderately perturbed (r_HH = 0.785 Å) relative to bare dihydrogen (r_HH = 0.754 Å), although the lengthening is still well outside the realm of dihydride complexes. In the
case of complex 6, the six equivalent H−H bonds exhibit lengths intermediate to these two limiting cases, at $r_{HH} = 0.770 \text{ Å}$. The Mg−H−H bond angle increases slightly, from 79.1° to 79.7°, as the ligand sphere increases from 1 to 6, which is consistent with the shortening H−H bond and the increasing distance from the metal center to the H$_2$ unit(s). Finally, the hydrogen ligands in [Mg(H$_2$)$_6$]$^{2+}$ are all oriented perpendicular to their nearest neighbors and parallel to the ligand opposite the metal center. This symmetric structure minimizes ligand interactions. All other structural details will be reserved for more substantive analysis in the context of nuclear motion in the following subsection.

**Nuclear Motion.** Analysis of the PIMD trajectories and statistical data suggests that these complexes are notably more fluxional than a static structure implies. The following discussion first examines the small complexes 1 and 2 in detail, in order to establish reference points and key structural parameters, and then presents trends across all structures through $n = 6$.

$[\text{Mg}(\text{H}_2)]^{2+}$. This triatomic species is reasonably limited in the amount of internal motion possible, but it also highlights structural properties contained within the metal−H$_2$ moiety alone. From the static structure calculations, complex 1 is known to exhibit the strongest interaction between the metal and ligand. The average H−H bond length from the PIMD simulations is $\langle r_{HH} \rangle = 0.812 \text{ Å}$, which is nearly 0.03 Å longer than the corresponding value in the static structure. Anharmonicity along the H−H stretch coordinate favors this lengthened bond and is apparent in the bond distribution shown in Figure 2. As expected, the quantum distribution for this high-frequency motion is more than twice as broad as the distribution from classical, thermal motion. The average distance from the metal center to the H−H bond is $\langle r_{\text{Mg−H}} \rangle = 2.088 \text{ Å}$, which is also longer than the static structure value of 2.036 Å. These two quantities appear at odds with one another, since a larger $r_{\text{Mg−H}}$ value would make the dihydrogen ligand more H$_2$-like and, therefore, exhibit a shorter $r_{HH}$. The resolution of this apparent discrepancy is that these coordinates are all strongly coupled via interaction with the metal center, and some component of anharmonic Mg−H stretch is involved in the admixture of H−H and Mg−H$_2$.

Tumbling/bending motion of the H$_2$ ligand is also active. While the average Mg−H−H angle (79.4°) is close to the static value (79.1°), the breadth of the distribution indicates that motion ±40° from the minimum structure is active. A 5.6 kcal/mol barrier prevents complete rotation along this direction, however. Rotation of the ligand about the axis between the metal and the H$_2$ bond midpoint is indistinguishable from overall rotation in complex 1, so discussion of this motion is reserved for the larger complexes. Overall, the quantum simulations provide a structural picture in which anharmonic zero-point motion of the H−H stretch lengthens this bond and in which large-amplitude angular motion of the dihydrogen ligand is active.

$[\text{Mg}(\text{H}_2)]^{2+}$. Addition of a dihydrogen ligand to complex 1 allows for examination of the relative motion of the ligands, as well as the many-body effect of distributing the cation’s influence over multiple ligands. The static structure 2 possesses H$_2$ ligands perpendicular to one another (dihedral angle $\phi_{\text{H}_2,H_2} = 90.6°$). While the quantum, thermal average matches this value, a single average value belies significantly active motion. The distribution of this dihedral angle is shown in the second panel of Figure 3. Nearly free rotation is observed. (The bias away from 0° and 180° is exacerbated by an angular distribution factor rather than a true structural bias.) Computation of the hindered-rotor transition state at the same level of theory exhibits a barrier of only 0.006 kcal/mol, which becomes ~0.06 kcal/mol upon inclusion of harmonic zero-point energy. This vanishing barrier is consistent with the absence of d back-bonding interactions and a concomitant lack of directional preference. Therefore, a more accurate depiction of the structure along this coordinate is a magnesium cation flanked by two fully active hydrogen propellers. The quantum and classical simulations produce very similar distributions along
The averaged values of angular coordinates show trends consistent with these changes in the dihydrogen ligands. As the $\langle r_\text{Mg-H} \rangle$ distance increases, for example, the $\langle \theta_\text{H-Mg-H} \rangle$ value decreases accordingly. The deviation of the averaged angular values from their static counterparts is small (although size-dependent), suggesting that this motion is reasonably harmonic. The value for $\langle \theta_\text{H-Mg-H} \rangle$ in complex 2 suggested that relative bending motions of the ligands were active. The averages in Figure 4 indicate convergence toward the vicinity of this dihedral coordinate. While the low frequency of this motion makes such a conclusion expected, the fact that the high-frequency dihydrogen stretches do not appreciably perturb the distribution indicates that the coupling between these two degrees of freedom is small.

Interestingly, the average angle between the centers of the ligands is found to be $\langle \theta_\text{H-Mg-H} \rangle = 136.4^\circ$. The bending motion of the ligands, relative to each other, is active. This average value is biased somewhat by a subtle geometric factor; the linear arrangement is a single point in the $\text{H}_2$ configuration space, whereas nonlinear arrangements carve out a cone. Nonetheless, the distribution in the third panel of Figure 3 demonstrates that bending motion is active over roughly 90°. The classical and quantum distributions exhibit nearly identical behavior; only the quantum distribution is shown in Figure 3.

Comparison to complex 1 suggests that $\langle r_\text{HH} \rangle$ is reduced in complex 2 by roughly the same amount as in the static structure, even though the PIMD quantity ($\langle r_\text{HH} \rangle = 0.808 \text{ Å}$) remains notably longer than in the static reference structure. The qualitative shape of the curves in the first panel of Figure 3 is nearly identical to the analogous plot in Figure 2. The angle between the metal center and the ligand bond is identical to the angle found for complex 2. The distance from the metal center to the midpoint of the ligand is also only slightly lengthened from its value in complex 1, although the lengthening is roughly double the change in the static structures. Therefore, the Mg–H$_2$ unit alone appears consistent with the qualitative structure found for 1, with the slightly shortened ligand and lengthened metal–ligand bond expected for the presence of two ligands. The relative motion of the two ligands is the unique feature of this complex. The low-frequency rotation and bending motions are highly active and contribute to large-amplitude motion of the dihydrogen ligands.

$\langle \text{Mg(H}_2\text{)}_3\text{]}^{2+}$. Additional dihydrogen ligands continue to create nonclassical σ complexes, as shown in static structures 3–6 of Figure 1. Remaining questions of structural flexibility in these complexes include the attenuating influence of the metal on the H–H bond, as well as the manner in which additional ligands inhibit or exacerbate dihydrogen motion. Statistically averaged structural values across the series of complexes are shown in Figure 4, with statistical distributions shown in Figure 5.

**Trends in Averaged Properties.** The $\langle r_\text{HH} \rangle$ values continue to decrease from complex 1 through complex 6, although they remain notably longer than the $r_\text{HH}$ values for the static structures (also shown in Figure 4 for reference). Since room temperature excitation of this high-frequency motion is unlikely, the broad distribution and long average bond length are ascribed purely to anharmonicity. Such anharmonicity is mainly induced by the presence of the metal center, which is confirmed by the fact that the same PIMD analysis applied to bare H$_2$ only increases the bond length from a static value of $r_\text{HH} = 0.754 \text{ Å}$ to $\langle r_\text{HH} \rangle = 0.779 \text{ Å}$.

The average distance from the metal center to the midpoint of the dihydrogen bond ($r_\text{Mg-H}$) also increases as the number of ligands increases. The source of this effect is the distributed influence of the metal cation over an increasing number of ligands. Since the ligand-dissociation coordinate becomes flatter as this effect occurs, the ligand can make larger anharmonic excursions from the metal center. Accordingly, the relative gap between the static and quantum results also increases during the 1–6 progression.

The averaged values of angular coordinates show trends consistent with these changes in the dihydrogen ligands. As the $\langle r_\text{Mg-H} \rangle$ distance increases, for example, the $\langle \theta_\text{H-Mg-H} \rangle$ value decreases accordingly. The deviation of the averaged angular values from their static counterparts is small (although size-dependent), suggesting that this motion is reasonably harmonic. The value for $\langle \theta_\text{H-Mg-H} \rangle$ in complex 2 suggested that relative bending motions of the ligands were active. The averages in Figure 4 indicate convergence toward the vicinity of the ligands. Since the ligand-dissociation coordinate becomes flatter as this effect occurs, the ligand can make larger anharmonic excursions from the metal center. Accordingly, the relative gap between the static and quantum results also increases during the 1–6 progression.
the static average (over all angles) of 108°. However, the distributions in the following section suggest that complete inhibition of bending does not occur. Finally, the dihedral angles between dihydrogen ligands remain near 90° throughout the complexes. That this value is observed over a range of molecular "shapes" in complexes 2–6 suggests that the ligands are undergoing essentially unhindered rotation.

**Trends in Property Distributions.** The distributions shown in Figures 2 and 3 highlighted the large-amplitude motion for smaller complexes, particularly in the H–H stretch and the relative motion of the ligands. Shown in Figure 5 are quantum distributions across the series of compounds for the same internal coordinates shown in Figure 4. The H–H bond distribution shifts to shorter distances for larger complexes, although the width of the distribution remains roughly constant. The Mg–H2 bond distribution, however, lengthens and expands in width. This observation is consistent with the growing gap between static and dynamic values shown in Figure 4. The bending angular coordinates, $\theta_{H-Mg-H}$ and $\theta_{Mg-H-H}$, do not provide any new qualitative insight beyond their average values, although these plots do serve to quantify the width of the distributions. The angular coordinates describing relative motion of the ligands contain much more information. The bending of the ligands relative to one another

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**Figure 4.** Statistically averaged structural properties for complexes 1–6. In each case, both classical MD and quantum PIMD results are depicted, and in the left panels, static bond lengths are shown. In the first panel, results for H2 are also included. Error bars throughout are smaller than the symbols in the plots, except for the lower-right panel, in which error bars are visible.

**Figure 5.** Quantum (PIMD) statistical distributions of structural properties for complexes 1–6. In the first panel, results for H2 are also included.
was established as an active coordinate in complex 2. This distribution shifts to smaller angles and eventually becomes bimodal for complexes 5 and 6, in accordance with the growing number of 90° angles in the latter compound’s static structure. The breadths of the two peaks indicate that the bending motion is, indeed, hindered in the more saturated complexes. Whereas complex 2 was making large-amplitude motions between 180° and 90° configurations, the larger complexes exhibit less bending flexibility due to the steric interactions with neighboring ligands. Finally, the dihedral distributions indicate that the propeller-like motions of the ligands remain active in the large complexes. Constrained potential energy scans along this rotor coordinate indicate that the motion of neighboring dihydrogen ligands is correlated, explaining the superimposed broad and 90° peaks in the distribution.

Given these structural trends, a reasonable question concerns the experimental observation of such properties. Mass spectrometry, as well as rotational and vibrational spectroscopy, of singly charged metal ions (ranging from Li+ to Cr3+) bound to a dihydrogen ligands has been studied both experimentally103−107 and computationally.105,108,109 Backing structural information out of these highly fluxional complexes is challenging, although such theory−experiment studies hold promise. These approaches should be extendable to the divalent ions, with additional ligands, and such experimental analysis is encouraged here.

**Isomeric Flexibility.** The static structures shown in Figure 1 were the only isomers that resulted from initial structural searches. The wealth of data from MD-based sampling provided an opportunity to search for additional minima accessed by the trajectories, however. By use of these data for species 3−6, 2000 structures were extracted from the sampling and subsequently “quenched” via geometry optimizations, followed by harmonic vibrational analyses. In order to analyze this large number of structures, rigid-body translation and (Euler angle) rotation were performed in order to optimally align the structures, using a root-mean-squared structural deviation (rmsd) as the optimization metric.

While several previously unidentified first- and second-order saddle points were discovered in this analysis, no energetically unique isomers were discovered. This result is consistent with the lack of d orbital interactions between the metal cation and the dihydrogen ligands; no spatial bias is imparted to the ligands in order to form energetically distinct isomers. An important exception, however, is the discovery of energetically equivalent (but symmetrically inequivalent) structural isomers. Two n = 3 isomers, for example, are shown in Figure 6 as superimposed, maximally aligned structures. In the original isomer (white hydrogens), the dihydrogen ligands each cant in a consistent orientation, relative to the average plane of the complex. The new isomer (silver hydrogens) behaves in the same fashion, but the hydrogens cant in the opposite direction. This change in angle can be obtained, physically, via internal rotation of the three ligands or, in the context of a symmetry analysis, via mirror-image reflection in several possible planes. Interestingly, this molecule, therefore, possesses a “handedness”, which is qualitatively similar to known tris-(ethylenediamine) metal coordination complexes.110 It exhibits a purely D3 point-group symmetry (not D3h or D3d). Similar H2-rotated isomers (not shown) were found in the larger complexes 4−6.

The MD/PIMD analyses, shown above, demonstrate that such symmetry considerations are likely immaterial to an understanding of the structure of this highly fluxional complex. The exquisitely low barriers to ligand rotation (as low as 0.01 kcal/mol, obtained via the quenching search) lead to unhindered rotation of the ligands and a thermal/quantum averaging of the resulting structures. The fact that energetically equivalent minima exist in these complexes is inherently connected to this rotational flexibility, however.

**Quantum vs Classical Motion.** The path integral methodology employed in this work provides a computationally tractable route for the potentially exact inclusion of quantum mechanical nuclear motion, including zero-point effects, thermal motion, and tunneling. For this series of complexes in the limiting σ-bound regime, an analysis of the role of such effects is worthwhile. The H−H bond distribution is found to be heavily quantum mechanical. Room-temperature thermal energy in this degree of freedom is roughly an order of magnitude smaller than the zero-point energy, so such a result was anticipated. The in−out motion of the dihydrogen ligands, relative to the metal center, was also found to be appreciably quantum mechanical. The remaining angular degrees of freedom, including the bending and propeller-like motions of the ligands, were all found to be suitably described by classical mechanics. This latter result is expected if these low-frequency coordinates are mostly decoupled from the more quantum mechanical high-frequency motions. In this series of complexes, results indicate that this decoupling, to a large extent, does occur. Such a decoupling would not be expected, for example, in species intermediate to the dihydrogen and dihydride ligand regimes.

### CONCLUSIONS

An analysis of the quantum mechanical motion of the complexes [Mg(H2)n=1−6]2+ has been performed using on-the-fly ab initio path integral molecular dynamics techniques. The results of these simulations suggest a notably dynamic molecular structure, which is qualitatively summarized in Figure 7 for two representative structures. The high-frequency H−H stretch is found to possess a moderately broad distribution, owing mainly to zero-point energy in an anharmonic potential. The bending motion of the dihydrogen ligands relative to the metal center (and relative to one another) is active in all species. Similarly, the propeller-like rotation about the metal−ligand axis is also found to be active, generally undergoing nearly unhindered rotation.

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**Figure 6.** Two unique structural isomers of complex 3 (viewed obliquely), which were obtained during the MD-based isomer search. The two structures (one visualized with darker hydrogen units) are maximally aligned via rigid-body translations and rotations, using an rmsd-based metric.
The role of such motions in influencing the binding (free) energies of these complexes has not yet been investigated. The anharmonic zero-point contributions and entropic factors (due to the active rotors) will putatively form the dominant deviations from static, harmonic analyses. Such motions would likely contribute nontrivially to metal–organic framework H₂ storage capacities, for example. Analyses of these factors will be performed in subsequent studies.

All of these low-frequency degrees of freedom exhibit large-amplitude motion within the coordination sphere of this strongly bound complex. This ligand-sphere mobility is the broader question to be addressed in dihydrogen, dihydride, and intermediate complexes, for which this study provides the first in a series of representative analyses. In canonical dihydrides, the H₂ bond is fully broken, whereas the M–H bond is stronger than in dihydrogen complexes. In the current study, the H₂ bond is still reasonably intact (apart from slight, anharmonic perturbations from the metal), whereas the M–H₂ bond is relatively weaker. The latter property was shown clearly in the M–H₂ bond averages and distributions of this work. No hydride/proton shuttling between neighboring ligand sites was observed, suggesting that a highly dynamic structure consisting of intact H₂ units is a reasonable qualitative picture of the compounds' structure. A remaining open question concerns the optimal amount of intrasphere mobility for either H₂ storage or hydrogenation catalysis purposes. This work has quantified the structure of a series of species in the σ-complex limiting regime and aims to serve as a useful reference point for future examinations of such mobility.

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