Rotational barrier of a molybdenum-molybdenum quadruple bond

(low-valent molybdenum–porphyrin complexes/variable temperature NMR)

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Contributed by James P. Collman, December 19, 1983

ABSTRACT The synthesis and characterization of molybdenum(II) porphyrin dimers containing unbridged metal-metal quadruple bonds are presented. Variable temperature 300 MHz 1H NMR studies of meso-substituted derivatives provide novel solution evidence for both the existence of quadruple bonds and for a barrier to rotation about the metal-metal bonds in these complexes. The activation energy for this rotational process is 10.1 ± 0.5 kcal mol⁻¹.

Transition metals (M) are capable of interacting in a mode that is unique in chemistry—that of forming quadruple bonds (1–3). This type of bonding can arise when the metals of two nearly planar d⁴ ML₄ fragments combine to form a binuclear complex. Spectroscopic (4) and theoretical (2, 5, 6) studies indicate that the metal-metal bonding in such complexes is mainly due to d-orbital overlap. A molecular orbital diagram derived from the valence d orbitals for a quadruply bonded M₂L₄ system (7, 8) is shown in Fig. 1A.

Based on molecular orbital theory (2, 9), the σ and pair of degenerate π bonds place no angular constraint on the orientation of the two ML₄ fragments. Only the δ bond should be sensitive to rotation about the metal-metal axis. The overlap of the dₓᵧ orbitals that gives rise to this bond is at a maximum when the two ML₄ fragments are eclipsed. Rotation of the ML₄ fragments about the metal-metal bond to form the staggered complex decreases this overlap. At a dihedral angle of 45°, the dₓᵧ orbitals effectively become nonbonding with respect to the metal-metal interaction as shown in Fig. 1B. Consequently, a quadruple bond should exhibit an electronic barrier to rotation about the metal-metal axis. The observation of such a barrier has not been previously reported.

Recently, it was suggested that rotation about a quadruple bond should not be observable on the NMR time scale due to the presence of the δ bond (10). This hypothesis may derive from early estimates based on electronic absorption spectroscopy, which place the strength of the δ bond in the range of 60–90 kcal mol⁻¹ (7, 8). However, structural evidence (11, 12) suggests that the δ bond provides only a minor contribution to the overall quadruple bond strength. Spectroscopic measurements by Trogler and Gray (4) support this latter view and place an upper limit of 20 kcal mol⁻¹ on the δ bond strength. It is interesting to note that one theoretical study predicts a rotational barrier of less than 1 kcal mol⁻¹ for a quadruple bond (13) and, in another case (14), the staggered geometry is predicted to be more stable than the eclipsed form by 4 kcal mol⁻¹.

Herein we report the synthesis and characterization of molybdenum(II) porphyrin dimers containing quadruple bonds and our investigation of the rotational barrier about the metal-metal bonds in these complexes.

MATERIALS AND METHODS

Visible spectra were recorded on a Cary model 219 spectrophotometer. NMR spectra were obtained from a 300 MHz Nicolet NMC-300 spectrometer, and all chemical shifts are reported relative to tetramethylsilane. IR spectra were measured on a Beckman Accumul 3 spectrometer or a Nicolet 7199 Fourier transform IR spectrometer. Mass spectroscopy (MS) was carried out on a Ribermag R-10-10-C mass spectrometer using electron impact ionization unless otherwise indicated. All manipulations of air-sensitive materials were performed in a Vacuum/Atmospheres (Hawthorne, CA) inert-atmosphere glove box or in Schlenkware.

All standard reagents were purchased and used without further purification. All solvents were rigorously dried by established methods (15) and distilled and stored under nitrogen. NMR solvents were vacuum transferred from sodium benzophenone ketyl. Deuterated toluene was used for variable temperature NMR experiments. Chromatographic silica gel and alumina were dried at 200°C and 0.01 mm for 20 hr. Octaethylporphyrin, H₂(EOP) (16), meso-formyloctaethylporphyrin, H₂(OEP-CHO) (17), meso-nitrooctaethylporphyrin, H₂(OEP-NO₂) (18), α,γ-dimethylenotriporphyrin-II, H₂(DMEtio) (19), and MoCl₆(CO)₄ (20) were prepared by literature methods.

Oxo(octaethylporphyrinato)molybdenum(IV), O=Mo(OEP), Compound 1, H₂(OEP) (560 mg, 1.05 mmol) and MoCl₆ (4.0 g, 15.2 mmol) were heated in degassed Decalin (200 ml) and octane (10 ml) under argon. After 6 hr

Abbreviations: M, transition metal; L, classical ligand such as halide, amine, pyridine, phosphine, etc.; Por, a general porphyrin dianion; DMEtio, the dianion of α,γ-dimethylenotriporphyrin-II; OEP, the dianion of octaethylporphyrin; OEP-X, mono-meso-substituted OEP, where X is formyl, nitro, amine, or isocyanate; MS, mass spectroscopy.
the mixture had turned dark wine red and a molybdenum mirror had formed on the sides of the reaction flask. The cooled solution was brought into the glove box, filtered, and passed down an 8-cm alumina column. A yellow-brown fraction was eluted with toluene and was discarded. Toluene/tetrahydrofuran, 20:1 (vol/vol) then was used to elute the magenta product band. Removal of the solvent under reduced pressure yielded 322 mg (43% based on porphyrin) of a purple solid. Recrystallization from toluene/octane afforded lustrous purple crystals. Visible (toluene) \( \lambda_{max} = 413 \text{ nm} \) (log \( \varepsilon = 5.33 \)), 540 (4.03), 578 (4.36), 644 (2.95); NMR (CD\(_2\)Cl\(_2\)) \( \delta \) H\(_{meso} \), 10.67 (s, 4H), CH\(_3\) 4.06 (m, 16H), CH\(_3\) 1.90 (t, 24H); MS m/e calculated 640–648. Found 640–649. Analysis calculated for C\(_{40}\)H\(_{38}\)N\(_2\)O: C, 76.07; H, 6.89; N, 8.69. Found: C, 67.40; H, 6.77, N, 8.61.

**Trans-Dichloro(octaethylporphyrinato)molybdenum-(IV),** Mo(OEP)Cl\(_2\), Compound 2. Under scrupulously oxygen-free conditions, O\(_2=\)Mo(OEP), compound I, (40 mg, 0.06 mmol) and trimethylsilylchloride (3 ml) were dissolved in toluene and stirred with gentle heating for 20 hr, during which a dark-brown precipitate formed. Filtration and washing with pentane produced 42 mg (97%) of dark-brown microcrystals. Visible (toluene) \( \lambda_{max} = 369 \text{ nm} \) (Soret), 400, 490; NMR (CD\(_3\)Cl) \( \delta \) CH\(_3\) 14.64 (q, 16H), H\(_{meso} \) 4.07 (br), CH\(_3\) 3.26 (t, 24H). MS m/e calculated: 694–706. Found: 694–707.

**Diphenylacetylene(octaethylporphyrinato)molybdenum-(II),** Mo(OEP)C\(_2\)H\(_4\), Compound 3. Mo(OEP)C\(_2\)H\(_4\), compound 2, (14 mg, 0.018 mmol) in toluene (20 ml) and a few drops of tetrahydrofuran was reduced with LiAlH\(_4\) in the presence of diphenylacetylene (Ph\(_2\)C=CPh) (14 mg, 0.079 mmol). After 1 hr of stirring, the dark-brown mixture turned dark red, and the solvent was removed under reduced pressure. The residue was chromatographed on a 4-cm silica flash column with toluene as the eluent. Removal of the solvent under reduced pressure yielded 16 mg (99%) of a dark-purple powder. Visible (toluene) \( \lambda_{max} = 406 \text{ nm} \) (Soret), 534, 564, 574; NMR (CD\(_2\)Cl\(_2\)) \( \delta \) H\(_{meso} \) 10.33 (s, 4H), m-p-phenyl 6.4 (m, 6H), o-phenyl 4.7 (m, 4H), CH\(_3\) 3.94 (q, 16H), CH\(_3\) 1.88 (t, 24H).

**Di(octaethylporphyrinato)molybdenum(II),** [Mo(OEP)]\(_2\), Compound 4a. Method 1. In the glove box, a Schlenk tube was charged with a benzene solution (6 ml) of Mo(OEP)(Ph\(_2\)C=CPh), compound 3 (26 mg, 0.03 mmol), sealed, and brought out of the box. The tube was cooled to −196°C and evacuated. The frozen solution was then warmed slowly, allowing the benzene to sublime from the tube, leaving an amorphous solid. Pyrolysis of this material at 20°C and 10⁻⁶ Torr produced a dark-brown powder (15 mg, 82%). Visible (toluene) \( \lambda_{max} = 356 \text{ nm} \) (log \( \varepsilon = 4.72 \)), 384 (4.86), 439 (4.56), 534 (4.01), 574 (3.76); NMR (CD\(_2\)Cl\(_2\)) \( \delta \) H\(_{meso} \) 9.20 (s, 4H), CH\(_3\) 4.32 (m, 8H) 3.92 (m, 8H), CH\(_3\) 1.77 (t, 24H); MS m/e calculated 1248–1264. Found 1248–1265. Analysis calculated for C\(_{72}\)H\(_{68}\)N\(_8\)Mo: C, 76.76; H, 7.07; N, 8.91. Found: C, 68.49; H, 7.23; N, 8.66.

**Method 2.** Under rigorously anaerobic and anhydrous conditions, H\(_2\)(OEP) (100 mg, 0.19 mmol) was dissolved in warm toluene (50 ml) and lutidine (2 ml). MoCl\(_3\)(CO\(_4\)) (500 mg, 1.79 mmol) was added, and the mixture was heated at reflux for 20 hr. If H\(_2\)(OEP) was detected by TLC (silica/toluene), another aliquot of MoCl\(_3\)(CO\(_4\)) was added, and heating was continued until no free porphyrin remained. The reaction mixture was then filtered, and the solvent was removed under reduced pressure. The resulting residue was flash-chromatographed on a 4-cm silica gel column in the glove box. The desired product was the brown first band eluted. Removal of the solvent under reduced pressure produced 4.70 mg (34%) of dark-blue powder. Recrystallization was accomplished from toluene/octane. This material was identical by MS, NMR, and visible spectroscopy to that prepared by method 1.

The following molybdenum porphyrin dimers were prepared using method 2. In some cases, a yellow component was coeluted with the product during chromatography. The dimers were easily purified by sublimation of the impurity at 80°C and 0.005 mm Hz.**
bonds of second and third row transition metals (21). The synthetic strategy used for the preparation of the molybdenum(II) dimer is shown in Eqs. 1-4.

\[
\begin{align*}
\text{Mo(CO)}_6 + \text{H}_2(\text{OEP}) &\rightarrow \text{O=Mo(OEP)} \quad [1] \\
\text{O=Mo(OEP)} + (\text{CH}_3)_3\text{SiCl} &\rightarrow \text{Mo(OEP)Cl}_2 \quad [2] \\
\text{Mo(OEP)Cl}_2 + \text{PhC》CPh} &\rightarrow \text{Mo(OEP)(PhC》CPh)} \\
2 \text{Mo(OEP)(PhC》CPh)} &\rightarrow \text{[Mo(OEP)]}_2 \quad [4]
\end{align*}
\]

The insertion of molybdenum into octaethylporphyrin is accomplished by a modified literature procedure (22) to produce the oxomolybdenum(IV) porphyrin, compound 1, which upon treatment with trimethylsilylchloride affords the trans-dichloride, compound 2. Reduction of this dichloride in a manner similar to that described by DeCiu et al. (23) for the meso-tetra-p-tolylporphyrin analog yields the Mo(II) diphenylethylene adduct, compound 3. Vacuum pyrolysis of the five-coordinate Mo(II) complex, compound 3, results in the formation of a product that we have characterized as a dimer (21), which should contain a formal molybdenum-molybdenum quadruple bond.

We subsequently developed an alternative procedure for the synthesis of molybdenum(II) porphyrin dimers. Heating a mixture of MoCl\(_2\)(CO)\(_4\) and H\(_2\)(Por) in oxygen-free toluene produces a substance which by NMR, visible, and mass spectroscopy is identical to the pyrolysis product, compound 4, of Eq. 4. Using this method, we have prepared a series of meso-substituted molybdenum(II) porphyrin dimers (Eq. 5).

\[
\text{MoCl}_2(\text{CO})_4 + \text{H}_2(\text{Por}) \rightarrow \text{[Mo(Por)]}_2 \quad [5]
\]

**Dynamic NMR Studies.** To establish further the nature of the bonding in these molybdenum dimers, we examined the meso-substituted derivatives by variable temperature NMR spectroscopy. Detection of geometric isomers would not only provide evidence for the presence of a quadruple bond but also could allow direct measurement of the barrier to rotation about the metal-metal bond.

The 300 MHz \(^1\text{H}\) NMR spectrum of [Mo(DMEtio)\(_2\)], compound 4b, exhibits a set of signals that is essentially temperature independent in the range from \(-95^\circ\text{C}\) to \(+80^\circ\text{C}\). This observation is consistent with three possibilities: (i) the two expected isomers are both present but are rapidly interconverting on the NMR time scale over the temperature range monitored, (ii) at some point, the two isomers slowly interconvert on the NMR time scale in this temperature range but fortuitously have identical chemical shifts, or (iii) one isomer thermodynamically predominates in solution. This last possibility seems unlikely because the presence of methyl sub-

**Fig. 2.** Low-temperature 300-MHz \(^1\text{H}\) NMR spectra of the formyl and meso proton regions of [Mo(OEP-CHO)]\(_2\).

stiuents on the porphyrin periphery should have little or no electronic or steric influence on the orientation of the porphyrin macrocycles.

To differentiate between the first two cases, it appeared evident that a meso-functional group that exhibits a large through-space magnetic anisotropy was needed. The formyl group proved to be a convenient spectroscopic label. Fig. 2 shows the formyl and meso regions of a series of variable-temperature 300-MHz \(^1\text{H}\) NMR spectra of [Mo(OEP-CHO)]\(_2\), compound 4c. At 20°C, exchange was rapid on the NMR time scale, resulting in an averaged spectrum that exhibited only a single formyl proton signal and a 2:1 pattern of nearly overlapping singlets for the meso proton resonances. As the temperature was lowered, the formyl signal gradually broadened and eventually separated into two singlets in a 1:2 ratio at \(-80^\circ\text{C}\). Similar behavior was observed for the meso proton signals, resulting in two new pairs of resonances that have an overall ratio of 1:2. This suggests the presence of only two NMR-detectable species at the slow exchange limit. However, for restricted rotation about the metal-metal quadruple bond of a disubstituted dimer, three isomers are possible at low temperatures in a statistical ratio of 1:2:1 as shown in Fig. 3. An alternative exchange mechanism involving rotation of the formyl group about the meso carbon bond also could result in a 1:2:1 mixture of atropisomers in the slow-exchange limit, as illustrated in Fig. 4. The activation barrier estimated from line-shape analysis (24) of 10.7 \(\pm\) 0.5 kcal-mol\(^{-1}\) is consistent with either exchange process. Note that if both processes have similar activation barriers, a maximum of nine sets of meso signals might be observed at low temperatures.

The low-temperature 300-MHz \(^1\text{H}\) NMR behavior of [Mo(OEP-NCO)]\(_2\), compound 4e, resembles that of [Mo(OEP-CHO)]\(_2\), compound 4c. From the variable temperature NMR dependence for [Mo(OEP-NCO)]\(_2\), an activation energy of 9.8 \(\pm\) 0.5 kcal-mol\(^{-1}\) was estimated. The similarity of

**Fig. 3.** Possible conformers due to rotation about the molybdenum-molybdenum bond. OEP macrocycle with only the meso-formyl groups shown.
the low-temperature NMR behavior and the activation energies for the two different derivatives is an indication that the same dynamic process is occurring for each dimer. Rotation about the metal-metal bond is most consistent with these observations and with the low-temperature 1:2 ratio of isomers. We attribute this distribution to the assumption that the "syn" isomer (Fig. 3) is a higher energy species due to dipolar interactions of the functional groups and, hence, is not significantly populated. This type of behavior has been observed for organic compounds (25). The remaining conformers apparently have equivalent free energies which thus lead to the observed 1:2 ratio at low temperatures.

A plausible assignment for the meso signals of disubstituted dimers in the slow-exchange limit is shown in Fig. 5. Our explanation for this pattern is based on the assumption that the meso functional group (X) provides a large through-space magnetic anisotropy that is manifested in a large downfield shift for the meso proton eclipsed to X. A small downfield shift appears to arise from through-bond effects transmitted from X to the γ meso proton in the same porphyrin.

To eliminate any possible intramolecular dipole effects, the mixed porphyrin dimer (OEP)MoM2Mo(OEP-CHO), compound 5, was prepared. A series of low-temperature 300-MHz 1H NMR spectra for this complex is shown in Fig. 6. At −90°C the slow-exchange limit is reached and a static structure is effectively observed. An important feature of these spectra is that the formyl and the meso proton resonances of the substituted porphyrin unit remain essentially unchanged throughout the entire temperature range. The low-temperature 1:1:2 meso proton pattern of the unsubstituted porphyrin fragment indicates that an eclipsed or near-eclipsed structure must be the major species in solution. As the temperature is raised, this 1:1:2 pattern gradually collapses into a singlet, unequivocally demonstrating that rotation about the metal-metal bond is the dynamic process observed. The rotational barriers measured for the three dimers are shown in Table 1. The question of formyl group rotation remains unanswered.

![Image](image-url)

**Fig. 5.** Proposed assignment for the low-temperature meso proton resonances of [Mo(OEP-X)]2. Newman-type projections down the molybdenum-molybdenum bond are illustrated. The OEP macrocycles are represented as circles with only the meso substituents shown for clarity.

**Fig. 6.** Low-temperature 300-MHz 1H NMR spectra of the formyl and meso proton regions of (OEP)MoM2Mo(OEP-CHO).

### SUMMARY

We have presented a detailed study of the variable temperature 1H NMR behavior of three different binuclear molybdenum(II) porphyrins. The observation of identical activation barriers, within experimental error, for the exchange exhibited by each dimer is an indication that the same dynamic process is occurring for all three complexes. Low-temperature 300-MHz 1H NMR data on the mixed porphyrin dimer, compound 5, unambiguously demonstrate that rotation about the molybdenum-molybdenum bond is the predominant process.

Because the δ overlap is the only metal–metal interaction that is ruptured on rotation about the molybdenum-molybdenum bond, the rotational barrier may serve as a measure of the δ bond strength. A 10-kcal-mol−1 δ bond energy is consistent with the spectroscopic measurement of Trogler and Gray (4) and lends some credence to this analysis. In addition, a similar correlation between the rotational barrier and σ bond strength of olefins has been made (26, 27). This leads to the possibility of addressing the controversy over the relative strengths of δ bonds in isostructural ditungsten and dimolybdenum complexes (28, 29). A measurement of the rotational barrier in tungsten(II) porphyrin dimers may help to resolve this discrepancy. However, we have so far been unable to prepare the tungsten analogs in pure form. Moreover, an important caveat involves the interpretation of the rotational barrier.

The degree to which this rotational barrier accurately reflects the δ bond strength depends on both steric and electronic factors. The intramolecular steric interactions between the porphyrin units can have two opposing consequences. The close proximity of the two porphyrin macrocycles could result in a repulsive effect that prevents the two ligated metals from achieving maximum δ overlap. Because this overlap is extremely sensitive to the metal-metal distance (2), such a situation would destabilize the ground state and, thus, decrease the rotational barrier. In contrast, nonbonding porphyrin interactions may further hinder rotation and result in a barrier height that overestimates the δ bond strength. It may be possible to probe this latter steric contribution.

<table>
<thead>
<tr>
<th>X</th>
<th>X'</th>
<th>ΔΔG°</th>
<th>kcal mol−1</th>
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<tr>
<td>CHO</td>
<td>CHO</td>
<td>10.7</td>
<td>± 0.5</td>
</tr>
<tr>
<td>NCO</td>
<td>NCO</td>
<td>9.8</td>
<td>± 0.5</td>
</tr>
<tr>
<td>CHO</td>
<td>H</td>
<td>9.8</td>
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Table 1. Activation energies for rotation about the metal-metal quadruple bond of (OEP-X)MoM2Mo(OEP-X')
bution to the rotational barrier by utilizing similar dynamic NMR techniques with substituted porphyrin dimers having bond orders of three or less, where no electronic restrictions on conformation should be possible. We have not yet examined such cases. However, two difficulties may be encountered with lower metal-metal bond orders. For example, in the triply bonded dimer, the porphyrin units should be farther apart and steric interactions should be correspondingly smaller. In addition, this NMR technique relies largely on a through-space magnetic anisotropy, which should diminish with the square of the interporphyrin distance. In any case, we believe that these steric effects may be alleviated by two structural characteristics expected of metalloporphyrin dimers (30): (i) the metals should be significantly displaced from the porphyrin framework towards each other, and (ii) the porphyrin skeletons should be domed away from each other.

An intriguing question concerns the nature of the $D_{4h}$ complex shown in Fig. 1B. Whether this species is a transition state or an intermediate during rotation about the quadruple bond is unknown. It is possible that overlap between the $d_{z^2}$ orbital of one metal and the $d_y^*$ orbital of the adjacent metal could stabilize this species. In addition, the two electrons occupying the degenerate, nonbonding $d_y^*$ orbitals of this staggered conformer can be paired or unpaired, resulting in the respective singlet or triplet spin states. Due to the presence of a heavy metal, intersystem crossing may be feasible during the time required for rotation about the metal-metal bond. Hence the magnitude of the singlet-triplet splitting and the extent of spin-orbit coupling could influence the barrier to rotation. Because these factors are unknown, the relationship between the rotational barrier that we have measured and the $\delta$ bond strength remains unclear.

Nonetheless, our results demonstrate that with little or no apparent steric complications, rotation about a molybdenum-molybdenum quadruple bond is a remarkably facile process at ambient conditions. Furthermore, the low-temperature 300-MHz $^1$H data are most consistent with molybdenum(II) porphyrin dimers having an eclipsed or near-eclipsed ground state geometry. Such structures are discordant with nonbonding steric interactions and accordingly constitute unique solution evidence for the existence of quadruple bonds.

We thank Professor Rick Finke for a generous gift of octaethylporphyrin; Professor John I. Brauman, Drs. William Lamanna and James Wright, and Messrs. William Tumas and Atsuo Kuki for helpful discussions; and Messrs. Pascal Michaud and Byron Wilson for some assistance in porphyrin syntheses. Financial support for this work was provided by National Science Foundation Grant CHE78-09443. NMR spectra were recorded on an instrument supported by National Science Foundation Grant CHE81-09664.