Spectroscopic Comparisons of MoW(porphyrin)₂ Heterodimers with Homologous Mo₂ and W₂ Quadruple Bonds: A Dynamic NMR and Resonance Raman Study

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Abstract: The rotational barrier for MoW(meso-monotolyl octaethylporphyrin)₂ ([TOEP]MoW[TOEP]) has been determined (ΔG̅rot = 10.6 ± 0.1 kcal/mol) by variable-temperature NMR and complete band shape analysis and is compared with values previously obtained for the analogous homodimers. The overall quadruple bond strengths of these isostructural dimolybdenum, ditungsten, and molybdenum–tungsten porphyrin dimers have also been compared by calculation of the force constants corresponding to each metal–metal bond stretching frequency as observed by resonance Raman spectroscopy. The Raman results are as follows: [Mo(OEP)]₂, νMoMo = 310 cm⁻¹, k = 2.72 mdyn/Å; [OEP]MoW(OEP), νMoW = 279 cm⁻¹, k = 2.89 mdyn/Å; [Mo-(TOEP)]₂, νMoMo = 310 cm⁻¹, k = 2.72 νMoMo [W(TOEP)], 3WW = 275 cm⁻¹, k = 4.08 mdyn/Å; and [(TOEP)-MoW(TOEP)], νMoW = 278 cm⁻¹, k = 2.87 mdyn/Å. Both the ¹H NMR and Raman spectra are consistent with a [(Por)MoW(Por)] structure wherein the Mo(Por) congener experiences a more drastic “bending-back” distortion of the porphyrin macrocycle.

Introduction

The first reported heteronuclear quadruple bonds between molybdenum and tungsten appeared to be some of the strongest bonds found in coordination complexes.¹ Cotton et al. have reported that the compound MoW(mhp)₄ (mhp = 2-hydroxy-6-methylpyridine anion) exhibits a larger force constant for the metal–metal stretch and a formally shorter bond length than either of the corresponding homodimers.² McCarley’s laboratory has also found a shorter bond in the MoW(O₂CCMe₃)₄ dimer relative to its homonuclear analogues.³ These observations led to a proposition that polar, heteronuclear metal–metal bonds exhibit a “special stability” relative to the homonuclear congeners.

More recently, the independent syntheses of MoWCl₄(PR)₃, (PR = PMePh₂, PMe₂Ph, or PMe₃) by Morris⁴ and McCarley⁵ provided the first family of unbridged molybdenum–tungsten quadruple bonds. The preliminary information available from electronic absorption spectroscopy,⁴ cyclic voltammetry,⁴ X-ray crystallography,⁶ photoelectron spectroscopy,⁷ and resonance Raman⁸ studies of these molecules suggests that the unbridged heteronuclear dimers exhibit properties which are the average of the homonuclear dimers. Evaluation of the apparently deviant properties of bridged heteronuclear dimers became the subject of a review by Morris,⁸ in which the “enhanced stability” of bridged heterodimers was attributed to ligand steric preferences.

We have recently developed a single-step preparation of the heterometallic porphyrin dimer [(OEP)MoW(OEP)] (1) containing an unsupported quadruple bond between molybdenum and tungsten. We report here the relative bond strengths for homologous dimolybdenum, ditungsten, and molybdenum–tungsten porphyrin dimers. The novel heterodimer [(TOEP)-MoW(TOEP)] (2) (TOEP = meso-4′-tolyl)octaethylporphyrin) has been synthesized to calculate the barrier to rotation about the mixed-metal δ-bond. Rotational barriers for [Mo(TOEP)]₂ (3) and [W(TOEP)]₂ (4) have been previously reported.⁹

Vibrational spectroscopy has been employed to determine PMoₚ and the corresponding force constants have been calculated for these same group VIB dimers. With these techniques a single component of the metal–metal quadruple bond as well as the overall multiple metal–metal bond may both be directly studied for evidence of an enhanced stability in the heteronuclear species.

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Experimental Section

Materials. H$_2$OEP and H$_2$TOEP were synthesized simultaneously by an adaptation$^{10}$ of the published procedure for H$_2$OEP.$^{11}$ Diethylylpyrrole was donated by Pharmacia and distilled immediately prior to use. Mo(CO)$_6$ and W(CO)$_6$, cobaltocene, and ferricinium hexafluorophosphate were purchased from Strem and distilled from sodium-benzophenone ketyl immediately prior to use. Solvents used for the metalation (Decalin) and manipulation (benzene) of the dimers were distilled from sodium benzophenone ketyl under argon before introduction into the glovebox. [Mo(OEP)]$_2$,$^{1,2}$[W(OEP)]$_2$,$^{13}$[Mo(TOEP)]$_2$,$^{10}$ and [W(TOEP)]$_2$,$^{10}$ were prepared according to published procedures.

Physical Measurements. A nitrogen-filled Vacuum Atmospheres drybox equipped with a Dri-Train inert gas purifier was employed for manipulations carried out under anaerobic conditions. $^1$H NMR spectra were recorded on a Varian XL-400 or General Electric 500 Omega FT-NMR spectrometer using benzene-d$_6$ or toluene-d$_8$ as a solvent. Resonances in the $^1$H NMR were referenced versus the residual proton signal of the solvent. The mixing time for the 2D NOESY/EXCHSY spectra was 100 ms. Resistance Raman samples were prepared in the glovebox and flame sealed under vacuum.

Excitation for the RR experiments was provided by an Ar$^+$ ion laser (Spectra Physics Model 171). Typical laser powers were 20–30 mW on resonance. Scattered light was collected by an f/1.5 5 cm focal length lens and focused onto the slit of a SPEX 0.6 operating as a spectrograph to detect the light onto a Photometrics CCD camera. Typical data acquisition times were 20 min. Because the precision of the depolarization ratios ($p$) was ±0.1, only general information such as whether bands were polarized ($p_{\parallel}$ modes), depolarized ($p_{\perp}$ modes), or anomalously polarized ($p_{a}$) could be determined.

Mass spectrometry was performed at the Mass Spectrometry Facility at the University of California—San Francisco and by Dr. Doris Hung of the Analytical Services Division at Northwestern University.

Preparation of 5-(4'-Methylphenyl)-2,7,8,12,13,17,18-octaeithyloporphyrin, H$_2$TOEP. A 3000 mL, three-neck, round-bottom flask was wrapped in aluminum foil and equipped with a Dean–Stark trap, stir bar, and argon inlet. The flask was charged with 3.4-diethylylpyrrole (5.00 g, 40.6 mmol) and 1500 mL of benzene and was sparged with nitrogen for 25 min. To this were added p-tolualdehyde (1.44 mL, 12.2 mmol), aqueous formaldehyde (2.76 mL of 37% solution, 34.7 mmol), and nitrogen for 25 min. To this were added benzene (2.74 mL, 0.379 mmol), W(CO)$_6$ (800 mg, 2.27 mmol), Mo(CO)$_6$ (100 mg, 0.468 mmol), W(CO)$_6$ (2.74 mL, 0.379 mmol), and a stir bar. The headspace was evacuated at 10$^{-2}$ Torr for 10–15 min to remove adventitious oxygen and water. The sealed flask was heated at 180 °C for 6 h, cooled to ambient temperature, and transferred to the glovebox and held at −20 °C overnight. (Caution! Although heating a closed system in this manner may often be hazardous and ill-advised, at this temperature the vapor pressure of Decalin is still less than 1 atm and the reaction is at a slightly negative pressure.) The mixture of [(TOEP)Mo(WOEP)] (I) (82 mg, 13.7%), [Mo(OEP)]$_2$ (917 mg, 34.1%), and [W(OEP)]$_2$ (6) (25 mg, 4.5%) was collected by filtration and washed with cold hexane. The ditiongustant species, 6, was removed as the monocation (EPR $g_{av}$ = 1.87) by titration of a benzene solution of the three dimers with a stoichiometric amount (5.80 mg, 0.0175 mmol) of ferricinium hexafluorophosphate (as determined by integration of Hmeso resonances in the $^1$H NMR and total mass of the mixture) followed by filtration and washing of the collected solid with benzene. [(TOEP)Mo(WOEP)]$^+$$^+$ ($^+$) was then isolated by a second titration with ferricinium hexafluorophosphate (16.1 mg, 0.0487 mmol) and collected by filtration and washed with benzene. The yield was 73 mg (9.8% based on porphyrin).

Results

$^1$H NMR: Rapid Rotation Regime. To be consistent with our previous study$^6$ of the rotational barriers for 3 and 4, we employed a single meso-tolyl substituent to break the characteristic 4-fold symmetry of octaethylporphyrin and divide the remaining meso-protons into two which are adjacent to the tolyl substituent, Hmeso, and one which is opposed, Hmeso'. The chemical shift difference between these meso-protons results from through-bond$^{14}$ and through-space contributions from the meso-tolyl substituent. A characteristic 2:1 set of meso-proton
Comparison of analogous $^1$H NMR spectra for 3 and 4 (Table 1) demonstrates that each corresponding resonance is located further downfield in the dimolybdenum species, 3. For this reason we find it reasonable to assign the more downfield sets in 2 to the molybdenum–porphyrin half of the dimer. Nonetheless, the distinctions between Mo(TOEP) and W(TOEP) resonances are not indisputable.

Molecular models and $^1$H NMR experiments$^{17}$ indicate that the tolyl rings in 2, 3, and 4 are positioned roughly perpendicular to the porphyrin plane as a result of steric interactions with the adjacent ethyl groups. The dynamic behavior of the $^1$H NMR is not complicated by tolyl atropisomerism. A meso-proton of one porphyrin which is eclipsed with the opposing meso-tolyl group is coplanar with the tolyl protons and is thus deshielded. This deshielding is very sensitive to the angle of rotation, and is negligible when the meso positions are staggered ($\chi = 45^\circ$).$^{10}$ A pronounced deshielding is only consistent with a conformation in which the meso positions of each porphyrin are eclipsed.

$^1$H NMR. Slow Rotation Regime. Peak broadening in the $^1$H NMR spectrum of 2 is significant immediately upon lowering the temperature below 20 °C. Figure 2 illustrates the dynamic behavior of the meso- and endo-α-tolyl bands in 2.

The H$_o$ doublets at $\delta$ 9.81 ppm (W) and 9.86 ppm (Mo) in Figure 1 are resolved into tw separate doublets each (W, $\delta$ 9.76, 9.90 ppm; Mo, $\delta$ 9.83, 10.0 ppm) in a ratio of 0.60:0.40 at low temperature. This observation suggests that, at $-70$ °C, 2 exists as a 1.5:1 ratio of two conformers: the dominant conformation with H$_o$ chemical shifts of $\delta$ 9.76 (W) and 9.83 (Mo) ppm, and the lesser populated conformation with chemical shifts of $\delta$ 9.90 (W) and 10.0 (Mo) ppm. The room-temperature spectrum is composed of time-averaged resonances derived from the chemical shift positions in these two conformations.

Analysis of the low-temperature meso-proton resonances is also consistent with the existence of two rotamers in a ratio of 1.5:1. Examination of the 2D NOESY/EXCHSY spectrum of 2 at $-78$ °C (Figure 3) enables a confident assignment of these two conformations as the anti and gauche eclipsed rotamers (see Figure 4). The off-diagonal resonances in the NOESY/EXCHSY spectrum of 2 may arise as a result of proton exchange between magnetically inequivalent positions or as a result of

Table 1. $^1$H NMR Chemical Shifts for Molybdenum and Tungsten Porphyrin Dimers

| compound          | $H_{\text{meso}}$ | $H_o$ | $H_m$ | $H_n$ | $H_{\text{CH}_2\text{CH}_3}$ | $H_{\text{CH}_2\text{CH}_3}$ | Ar-CH$_3$
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<td>10.07</td>
<td>8.06</td>
<td>7.00</td>
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<td>7.10</td>
<td>3.76</td>
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<tr>
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<td>9.41/9.19 (Mo)</td>
<td>9.91</td>
<td>7.95</td>
<td>6.98</td>
<td>9.91 (Mo)</td>
<td>7.95 (Mo)</td>
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<tr>
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<td>8.97/8.81 (W)</td>
<td>9.86</td>
<td>7.95</td>
<td>6.98</td>
<td>6.98 (W)</td>
<td>2.59 (W)</td>
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<tr>
<td>[(TOEP)MoW(TOEP)]</td>
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</table>

*a Multiplets.

Figure 1. (a) meso-Proton regiochemistry in monosubstituted OEP derivatives. (b) Aryl proton regiochemistry in metalloporphyrin dimers. (c) $^1$H NMR of 2 (C$_6$D$_6$, 20 °C).

Resonances for each half of the heterodimer, [(TOEP)-MoW(TOEP)] (2). The room temperature $^1$H NMR spectrum for 2 is shown in Figure 1. Figure 1c also consists of bands readily assigned to the tolyl groups and the β-ethyl substituents. The endo-tolyl protons (H$_e$ and H$_n$), which are directed across the metal–metal bond, are much more strongly deshielded than the exo-protons (H$_o$ and H$_m$). Quantitative calculations of the diamagnetic anisotropies ($\Delta\chi$) of Mo$_2$, W$_2$, and MoW quadruple bonds confirm the largest $\Delta\chi$ values yet reported, over 1 order of magnitude greater than the $\Delta\chi$ values obtained for alkynes.$^{15}$ As seen in Figure 1, the H$_o$ resonances in 2 are shifted downfield by nearly 3 ppm relative to H$_n$.$^{16}$


(16) The change in chemical shift, $\Delta\delta$, is related to $\Delta\chi$ by $\Delta\delta = (\Delta\chi/4\pi r^2)(1 - 3 \cos^2\theta/\sin^2\theta)$, where $r$ is the distance of the test nucleus to the source of anisotropy and $\theta$ is the angle between the $r$ vector and the source axis.

(17) A significant shielding of the methylene protons in the ethyl groups adjacent to the tolyl substituent is observed ($\delta$ 3.00 and 2.83 vs 4.6-3.8 ppm for 2, Table 1), analogous to shifts in [10]paracyclophanes: Agarwal, A.; Barnes, J. A.; Fletcher, J. L.; McGlinchey, M. J.; Sayer, B. G. Can. J. Chem. 1977, 55, 2575.
through-space interactions (nuclear Overhauser effect) between separate protons. There are 12 off-diagonal resonances observed in Figure 3. Of these, four (labeled N1–N4) must be a result of NOE since they relate an endo-tolyl H′ proton to a meso-proton. The existence of NOE cross-peaks between endo-tolyl H′ protons and meso-protons, but not between endo-tolyl H′ protons and β-ethyl protons, is consistent with our claim that the two low-temperature limit rotamers are eclipsed. The two farthest downfield meso-proton resonances, at δ 9.71 and 9.52 ppm, are assigned as Mo H1 and Mo H3 according to the scheme in Figure 4. This assignment is made on the basis that Mo-(porphyrin) protons should be downfield of corresponding W(porphyrin) protons (see Table 1) and protons eclipsed with the opposing tolyl substituent should be downfield of protons eclipsed with opposing meso-protons. The relative intensities of Mo H1 and Mo H3 indicate that H1 belongs to the less populated anti rotamer, and H3 to the more populated gauche rotamer. Interestingly, W H1 and W H3 have slightly different chemical shifts at –60 °C (see Figure 2), but accidentally overlap in the limiting low-temperature spectrum. Nonetheless, the separate cross-peaks labeled N3 and N4 in Figure 3 identify their respective locations at δ 9.28 and 9.27 ppm.

The remaining off-diagonal resonances, labeled E1–E8 in Figure 3, may be used to identify the chemical shift positions of the remaining protons in Figure 4. As the anti rotamer exchanges with the gauche, Mo H1 should exchange with Mo H5. Figure 3 demonstrates a cross-peak (E3) which relates Mo H1 to a third resonance buried underneath W H1 and W H3. Thus, the chemical shift position of Mo H5 is determined to be δ 9.27 ppm. Likewise, Mo H3 and Mo H4 should become degenerate at a new chemical shift (Mo H2) as the gauche rotamer returns to the anti. The NOESY/EXCHSY spectrum demonstrates an exchange peak (E4) for Mo H3 with the resonance at δ 8.99 ppm. Because Mo H4 and Mo H2 are both H cis and both eclipsed with meso-protons, they exhibit no noticeable chemical shift difference and the cross-peak relating Mo H4 to Mo H2 is located along the diagonal (E5).

Similar reasoning enables assignment of the five W meso bands. Cross-peak E6 relates W H1 to W H5, and cross-peak E7 relates W H1 to W H2. Finally, W H4 is also exchanged with W H2, but in contrast to Mo H4 and Mo H2, the tungsten protons are slightly resolved at the low-temperature limit. Nonetheless, the cross-peak relating W H4 and W H2, E8, is still located near the diagonal. Cross-peaks E1 and E2 are the result of H trans exchange between the two rotamers.

The pattern of meso-proton assignments at the low-temperature limit (Figure 5) is solely consistent with population of the two eclipsed rotamers as shown in Figure 4. The relative intensities of each peak are also in good agreement with the calculated values according to populations of 40% anti and 60% gauche rotamers (Table 2). Further support for the eclipsed ground-state assignments is provided by the close agreement of the observed chemical shift difference between H1 and H3 (Mo, 0.45 ppm; W, 0.47 ppm) and the calculated maximum deshielding expected for a tolyl group which is perfectly eclipsed with a meso-proton (0.47 ppm). These two protons provide an ideal measure of the deshielding as both H1 and H3 are H trans.

![Figure 2](image2.png) Variable-temperature 1H NMR at 500 MHz of 2. Rates determined by complete band shape analysis.

![Figure 3](image3.png) 500 MHz 2D NOESY/EXCHSY spectrum of 2 at –78 °C (toluene-d8).

![Figure 4](image4.png) Eclipsed rotational isomers about a quadruple metal–metal bond showing the meso-proton labeling scheme used in the text. The two metalloporphyrin halves of the dimer are labeled separately for each rotamer (anti on the left, gauche on the right). In this work X = tolyl groups only.

(19) The complete NOESY/EXCHSY spectrum is available as Supporting Information.
(20) H1 and H2 are both eclipsed with opposing tolyl substituents; however, H1 is trans to its own tolyl substituent and H2 is cis. Studies of similar OEP-X porphyrin complexes indicate that Htrans protons are located downfield of Hcis protons.
but H₁ is eclipsed with the tolyl group while H₅ is not. This agreement is very good evidence in support of an eclipsed geometry between the meso-protons and the tolyl substituents.

The 1.5:1 ratio of gauche:anti eclipsed rotamers in 2 is nearly identical to the ratios previously determined for 3 and 4. Deviation from the purely statistical ratio of 2:1 is consistent with a slight thermodynamic preference (≤ 2 kcal/mol) for the anti conformation. In all three cases the syn rotamer, with tolyl substituents eclipsed, is not populated to any detectable extent. Exclusion of the syn rotamer is not surprising since models have shown the tolyl protons to extend across the metal—metal bond to within 0.15 Å of its center. Such an orientation would result in severe tolyl—tolyl repulsive interactions and accounts for the absence of the syn rotamer in all three metalloporphyrin dimers studied.

**Δ-Bond Rotational Barrier. Low-Temperature Limiting Spectrum Method.** A first estimate of the rotational barrier for 2 is possible through identification of the temperature, T₁, when line broadening of the low-temperature limiting spectrum just becomes perceptible. This method has been presented by Fuller as an alternative to coalescence point analysis (CPA). CPA is dependent on the chemical shift difference (Hz) between sites in the absence of exchange, and thus varies with the field strength of the spectrometer. Not only are a variety of spectrometer field strengths now in use, but the chemical shift differences between sites for meso-protons and endo-tolyr protons at the low-temperature limit are not the same. Coalescence point analysis would yield several different rotational barriers for the same molecule, and for these reasons its use is not recommended by the authors.

Initial broadening of the tolune-d₆ ¹H NMR spectrum of 2 is seen at −80 ± 5 °C. This value of T₁ results in a ΔG°ₗₗ = 10.7 ± 0.3 kcal/mol.²²

**Complete Band Shape Analysis.** The meso, H₅, and H₆ protons of 2 provide eight separate spin systems (H₅cis, H₅trans, H₆, and H₆ for each metal) that may be analyzed through complete band shape analysis (CBA). As each spin system is characterized by a separate set of spectral parameters, a multiple verification of rate results from the best fit of all simulations at a given rate. The rates corresponding to each variable-temperature spectrum have been listed in Figure 2.²³ The barrier for interconversion of the anti and gauche rotamers (ΔG°ₗₗ = 10.6 ± 0.1 kcal/mol), determined from an Eyering plot²⁴ of the best-fit rates versus 1/T (Figure 6), is in excellent agreement with the low-temperature limiting spectrum analysis. The very low value of ΔS°ₗₗ renders this barrier temperature independent, within experimental error: ΔG°ₗₗ = ΔH°ₗₗ.

**Vibrational Spectroscopy.** The three meso-tolyl octaethyl-metalloporphyrins (2, 3, and 4) which have been investigated by dynamic NMR¹⁰ (vide supra) have also been characterized by resonance Raman spectroscopy. In each case enhancement of a mode assigned as the metal—metal stretch was effected with UV-excitation (363.8 nm) into the blue side of the dimer Soret band (see Figure 8). Assignment of the ν₉₉₉ modes was made on the basis of similar vibrational studies of other quadruply bonded group VIB dimers,⁵ depolarization ratios, and subtraction of the spectrum obtained from the corresponding metalloporphyrin monomer. Enhancement of the metal—metal stretch in this fashion is consistent with the enhancement mechanism which has been proposed for axial-ligand vibrational modes in resonance with the Soret band of many other metalloporphyrins. A change in the internuclear distance of the metal—metal bond could occur either via overlap of the 2s₉₉₉ (23) Rates were calculated with the program DNMR 5, obtained from Dr. Richard Counts at the Quantum Chemical Program Exchange, Indiana University, and adapted for use on a desktop PC. Transverse relaxation times, T₂, were obtained at each temperature from the line widths in [(OEP)Mo(W(0EP)),] which undergoes the same dynamic exchange but between sites which are magnetically equivalent. (24) The formula −ln(ΔT) = −ln(Kb/h) + ΔG°/RT is the Eyering equation, where K is the transmission coefficient, h the Boltzmann constant, and b Planck’s constant. See: Sandstrom, J. Dynamic NMR Spectroscopy; Academic Press: New York, 1982. (25) (a) Cotton, F. A.; Walton, R. A. Multiple Bonds Between Metal Atomes; Wiley: New York, 1993; pp 735–739. (b) Tait, C. D.; Garner, J. M.; Collman, J. P.; Sattelberger, A. P.; Woodruff, W. H. J. Am. Chem. Soc. 1989, 111, 9072–9077. (26) RR spectra were also obtained for the monomers Mo(TOEP)(O) and W(TOEP)(O)(Cl). The modes assigned as ν₉₉₉ in the dimers were absent from the monomer spectra.
porphyrin orbital with the metal–metal σ-bond, or via overlap of the porphyrin $3e_g^\pi$ orbital with the metal–metal $\pi^\sigma$-bonds. The change in electron density on the porphyrin that accompanies the ring-centered $\pi \rightarrow \pi^\sigma$ Soret transition may thus result in a change in electron density and hence bond length of the metal–metal bonded axial ligand.

**Table 3.** Calculated Structural Parameters from Observed M–M Stretching Frequencies

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*The bond lengths (D) have been estimated from an empirical relationship (ref 28), which gives distinct formulas for second and third row homodimers. Both results have been presented for the MoW heterodimers.

Table 3 summarizes the structural parameters calculated from the metal–metal bond vibrational data for several metalloporphyrin dimers. Force constants were obtained from the diatomic oscillator approximation, and metal–metal distances were estimated using an empirical correlation between force constants and metal–metal bond lengths.

Spectra of [(OEP)MoW(OEP)] (1) and [Mo(OEP)]$_2$ (5) were also obtained to determine the validity of the diatomic approximation wherein ligand effects (such as mass) are neglected in the calculation of metal–metal bond force constants. Figure 7 shows the low-frequency region of the RR spectra for 1, 2, 3, 4, and 5. Our results indicate that the substantial difference in ligand mass between the OEP and TOEP porphyrin dimers has a relatively small effect on the metal–metal bond stretching frequency. The shift for the two Mo–Mo stretches is at most 1–2 cm$^{-1}$, and the shift for the Mo–W stretches is at most 2–3 cm$^{-1}$, both to lower frequency for the TOEP dimers.

Several other lines of evidence are also consistent with our assumption that the metal–metal stretch is essentially M$_2$ localized. The metal–nitrogen force constant is very weak relative to the metal–metal force constant; thus, mixing of metal–nitrogen stretching or metal–metal–nitrogen bending coordinates with the metal–metal stretch coordinates is limited. The same may not be said for analogous M$_2$X$_4$(PR$_3$)$_2$ dimers, since in those molecules the metal–halide force constant is comparable in magnitude with the metal–metal force constant. To estimate the exact percentage of localized diatomic character exhibited by the metal–metal stretches in M$_2$(OEP)$_2$ dimers, we have performed a simple normal coordinate analysis (see the Supporting Information) with the structural parameters from our single-crystal X-ray diffraction study of [Ru(OEP)]$_2$. The results from this study indicate that only minor systematic corrections of a 10% or less reduction in the force constant need to be applied to the diatomic oscillator approximation used to describe metal–metal bonding between second and third row metals in porphyrin systems. These studies and the small mass

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(27) $k = (3.55 \times 10^5) \mu \nu^2$, where $k$ = force constant (mdyn/Å), $\mu$ = reduced mass of the two metal atoms (g), and $\nu$ = vibrational frequency (cm$^{-1}$).


The appropriate equation for elements Rb–Xe is $D_{AM} = 1.83 + 1.51 \exp(-2.48D)$, where $D$ is in Å and $k$ is in mdyn/Å. For elements Cs–Rn, $D_{AM} = 2.01 + 1.31 \exp(-4.28D)$.

(29) Quality spectral data were not obtained for W$_2$(OEP)$_2$, probably due to its very poor solubility, so a third comparison is not available.

effect seen upon substitution of TOEP for OEP provide good support for the trend observed in Table 3. The Raman data indicate that the force constants increase in the order Mo–Mo < Mo–W < W–W, implying a trend in overall metal–metal bond strength that places the heterodimer intermediate between the two homodimers, but significantly weaker than their calculated average.

In addition to the Soret, the electronic absorption spectra of 2, 3, and 4 exhibit an intense band at 430–440 nm (Figure 8). Although the metal–metal stretching band is strongly enhanced with excitation at 363.8 nm, it is not seen upon excitation at 432, 439, 457, 476, or 488 nm (Raman data not shown). These excitation wavelengths span the electronic transition at 438 nm and were performed to understand the scattering mechanism which gives rise to the observed metal–metal stretch. The most well-supported hypothesis is that the 438 nm band is a ligand–metal charge transfer from the porphyrin HOMO (3ε_g*) to the δ⁺*(b1u) orbital, but we have not confirmed the assignment by identification of an associated MCD A term.

The porphyrin skeletal vibrations observed in the frequency range 1470–1610 cm⁻¹ in the meso-tolyl-substituted OEP dimers 2, 3, and 4 are similar upon excitation into either absorption band. Vibrational assignments of the porphyrin skeletal modes were inferred from the depolarization ratios and from comparisons with the vibrational spectra of Ni(OEP)³¹ and [Ru(OEP)]².³² The Ni(OEP) monomer is a very useful standard for comparison since a complete normal coordinate analysis has been correlate with the spectra,³³ and the vibrational numbering scheme for OEP vibrations was developed for this compound. The similarity of metalloporphyrin dimer spectra with metalloporphyrin monomer spectra is consistent with previous studies. The vibrational peak positions of [Ru(OEP)]² are almost identical to those in Ru(OEP)(CO),³² and even stacked silicon phthalocyanine vibrations are not shifted significantly from the silicon phthalocyanine monomer.³⁴

Figure 9 shows the high-frequency region of the RR spectra for 2, 3, and 4 obtained with excitation at 432 nm. The extreme complexity of these molecules has precluded us from performing complete, high-frequency region normal-mode analyses and thus being able to assign each of the observed porphyrin skeletal modes according to the scheme in ref 33. However, the overall qualitative picture which emerges upon inspection of Figure 9 demonstrates a striking similarity between the high-frequency spectra of Ni(OEP) and [W(TOEP)]². In contrast, the dimolybdenum spectrum appears as a superposition of the homodimer spectra. These features are consistent with a greater “bending-back” distortion of molybdenum–porphyrin entities, while tungsten–porphyrins resemble the four-coordinate, planar Ni(OEP). The mixed-metal dimer appears to exhibit both features simultaneously.

The ¹H NMR spectra of 2, 3, and 4 are also consistent with this structural difference between molybdenum– and tungsten–porphyrin complexes. The chemical shift difference of Hcis and Htrans is dominated by the through-space magnetic anisotropy of the opposing tolyl group. Assuming exchange between eclipsed ground state conformations, the magnitude of deshield-


Discussion

We have estimated the δ-bond strengths of isostructural Mo₂, W₂, and MoW porphyrin dimers by measuring the barrier to rotation about the metal–metal bond. Historically, δ-bond strengths have been correlated with δ − δ⁺ electronic transition energies.³⁵ Such studies imply stronger δ-bond strengths for the dimolybdenum verses ditungsten quadruple

bonds,\textsuperscript{36} in striking contrast to our results. However, recent reports\textsuperscript{37} have indicated that several factors must be considered in the analysis of $\delta \rightarrow \delta^*$ electronic transition energies. Such factors include the amount of metal–ligand $\delta$-bonding,\textsuperscript{38} the degree to which configuration interaction is involved in the ground state,\textsuperscript{39} and mixing of the $\delta \rightarrow \delta^*$ transition with metal-to-ligand charge transfer (MLCT) bands.\textsuperscript{40} These studies conclude that simple correlations should not be made between $\delta$-bond strength and $\delta \rightarrow \delta^*$ energies.

Measurement of the rotational barrier for quadruply bonded complexes is an accurate, direct method for estimation of the $\delta$-bond strength. The $\sigma$ and $\pi$ contributions to the quadruple bond are cylindrically symmetrical, and hence exhibit no angular preferences for overlap. However, the $\delta$-bond achieves maximum overlap in an eclipsed conformation, and is completely nonbonding when the $d_{xy}$ orbitals are staggered at 45°. Since exchange between the anti and gauche eclipsed conformations of metalloporphyrin dimers such as 2, 3, and 4 requires a staggered transition state (see Figure 11), the rotational barrier, $\Delta G^\circ_{\text{rot}}$, is an accurate estimation of $\Delta G_3$ in the absence of ligand steric contributions ($\Delta G^\circ_{\text{rot}} = \Delta G_3 - \Delta G_2$). Previous rotational barrier studies\textsuperscript{41} of [Mo(OEP-X)]\textsubscript{2} with linear substituents (X = formyl, isocyante, and NH2) all indicate a barrier to rotation which is within experimental error of that observed for [Mo(ToEP)]\textsubscript{2}. Insensitivity of these rotational barriers to the incorporation of meso-aryl substituents allows an estimation of $\Delta G_3$ (≤0.5 kcal/mol).\textsuperscript{42}

Comparisons may now be made between the overall quadruple bond strengths for Mo\textsubscript{2}, W\textsubscript{2}, and MoW as well as between $\delta$-bond strengths for the same molecules. Metal–metal quadruple bond force constants indicate that the ditungsten species, 5, contains the strongest quadruple bond (Table 3). This result is consistent with our rotational barrier studies, which likewise suggest that the ditungsten $\delta$-bond is also stronger than either dimolybdenum or molybdenum–tungsten (Table 4).

As shown in Table 3, empirical equations derived from vibrational data predict that the W\textsubscript{2} and Os\textsubscript{2} bonds are shorter than the metal–metal bonds in isoelectronic Mo\textsubscript{2} and Ru\textsubscript{2} congeners. Many pairs of homologous Mo\textsubscript{2} and W\textsubscript{2} dimers have been structurally characterized, including the tetraphenylporphyrin dimers ([Mo(TPP)]\textsubscript{2})\textsuperscript{43} and [W(TPP)]\textsubscript{2});\textsuperscript{44} and in every case the W\textsubscript{2} bond length is about 0.10 Å longer than the corresponding Mo\textsubscript{2} bond length.\textsuperscript{25} Although the empirical equations have proved extremely accurate with the ligand systems from which they were derived, the equations may simply not be applicable to porphyrin dimers. Calculated force constants for the W\textsubscript{2} and Os\textsubscript{2} porphyrin dimers are 25–35% larger than the corresponding values for Mo\textsubscript{2} and Ru\textsubscript{2} dimers. The magnitude of this difference is by far the largest yet observed; indeed, the ligand systems used to generate the empirical equations exhibit force constant changes of only 4–8% upon substitution from Mo–Mo to W–W.\textsuperscript{25} However, most of these ligand systems bridge the metal–metal bond, and thus may be expected to greatly affect the strength of the metal–metal bond through their own steric restraints and electronic preferences. The large dependence of force constant on metal identity in our systems may well be a result of the unbridged, unrestrained nature of the metal–metal bond. That the metal–metal stretches in metalloporphyrin dimers are essentially M\textsubscript{2} localized is also supported by a detailed analysis given as Supporting Information. Normal-mode calculations therein indicate that the contribution of metal–metal motion to the potential energy distribution (PED) of the vibrations assigned

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Dimer & $\Delta G^\circ_{\text{rot}}$ \\
\hline
[(TOEP)MoW(TOEP)] & 10.6 ± 0.1 \\
[Mo(TOEP)]\textsubscript{2} & 10.8 ± 0.1 \\
[W(TOEP)]\textsubscript{2} & 12.9 ± 0.1 \\
\hline
\end{tabular}
\caption{Comparison of $\Delta G^\circ_{\text{rot}}$ for [Mo(TOEP)]\textsubscript{2}, [Mo(WTOEP)]\textsubscript{2}, and [W(TOEP)]\textsubscript{2}.}
\end{table}
as \( \nu_{\text{MM}} \) are on the order of 80–90%. The nearly complete isolation of the metal–metal stretch in these molecules may be understood as a consequence of the relatively large mass of the metal atoms, relatively strong metal–metal bond, and relatively weak metal–porphyrin stretching and bending interactions.

Despite the preponderance of evidence suggesting that third row metals form significantly stronger bonds than second row metals, in neither the rotational barrier nor the vibrational studies is the dimolybdenum bond significantly strengthened by substitution of a single tungsten atom. Table 3 manifests a small increase in quadruple bond strength for MoW relative to the Mo\( _2 \) species; however, Table 4 demonstrates the presence of a slightly weaker MoW \( \delta \)-bond.

Molecular orbital theory predicts that the bond strength, \( \Delta E \), of a metal–metal bond will be dominated by two factors. The interaction energy will be made larger as the atomic orbitals achieve more geometric overlap via incorporation of more diffuse orbitals. However, \( \Delta E \) is a maximum when the initial energies of the interacting orbitals are identical. Previous heterodimer studies\(^8\) have not directly addressed how the strength of a heterodimeric metal–metal bond is affected by the difference in atomic orbital energy levels. Greater electronegativity of Mo\( ^{11} \) relative to W\( ^{11} \) lowers the energy levels of its atomic d-orbitals (Figure 12). Molecular orbital theory predicts that mismatch of the atomic orbital energies will have a deleterious effect on the interaction energy for formation of the heteronuclear bond.

The face-to-face nature of \( d_{xy} \)–\( d_{xy} \) overlap does not make effective use of the radially diffuse third row \( d_{xy} \) orbital. Thus, the MoW \( \delta \)-bond is slightly weakened from the homonuclear Mo\( _2 \) congener upon incorporation of the lower energy W 5\( d_{xy} \) orbital. This slight weakening occurs despite the increased radial distribution of the 5d \( d_{xy} \) orbital. In contrast, the \( \sigma \)- and \( \pi \)-bonds are composed of atomic d-orbitals which have their distribution maxima directed toward each other, as opposed to the face-to-face orientation required for \( \delta \)-bond formation. Direct orientation of the \( d_{z^2} \) and \( d_{x^2} \, d_{y^2} \) orbitals enables a more efficient utilization of the more diffuse 5d orbitals for \( \sigma \)- and \( \pi \)-bonding, hence, the force constant\(^{45}\) for the overall quadruple bond in MoW is increased from its value in Mo\( _2 \). The same result is seen in the resonance Raman studies of MoW(\( \text{Cl} \)\( _4 \))(PM\( \text{e} \_3 \)\( _4 \)) and Mo\( _2 \)(\( \text{Cl} \)\( _4 \))(PM\( \text{e} \_3 \)\( _4 \)).\(^3\)

Repeated attempts to obtain X-ray suitable single crystals of the quadruple bonded metalloporphyrin dimers have been unsuccessful. Such a study may be expected to reveal a bond length for MoW which is slightly increased from the average lengths of Mo\( _2 \) and W\( _2 \). Although not available for the porphyrin dimers, Morris has reported the crystal structure for MoW(\( \text{Cl} \)\( _4 \))(PM\( \text{e} \_3 \)\( _4 \)) and Cotton has determined analogous structures of Mo\( _2 \)(\( \text{Cl} \)\( _4 \))(PM\( \text{e} \_3 \)\( _4 \)) and W\( _2 \)(\( \text{Cl} \)\( _4 \))(PM\( \text{e} \_3 \)\( _4 \)).\(^{46}\) The M–M bond distances increase in the order Mo\( _2 \) (2.130 (0) Å) < MoW (2.2092 (7) Å) < W\( _2 \) (2.262 (1) Å). Indeed, the MoW bond length is approximately 0.015 Å longer than the average of the homodimers, consistent with our comparison of the three \( \nu_{\text{MM}} \) force constants for 2, 3, and 4.

**Conclusions**

The rotational barrier (\( \Delta G_{\text{rot}}^\ddagger = 10.6 \pm 0.1 \text{ kcal/mol} \)) and metal–metal bond force constant (\( k = 2.87 \text{ mdyn/Å} \)) have been reported for the mixed-metal dimer [(TOEP)MoW(TOEP)]. The results indicate the existence of competing effects on the determination of heterometallic bond strengths. Atomic orbital energy mismatch due to a difference in metal atom electronegativities causes a net loss of Mo \( d_{xy} \)–W \( d_{xy} \) interaction energy

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(45) Estimates indicate that the \( \delta \)-bond contributes only about 10% of the overall bond strength; therefore, trends in the quadruple bond force constants will be primarily indicative of changes in the \( \sigma \)- and \( \pi \)-bond strengths.

and thus a δ-bond which is slightly weaker in MoW than in either Mo₂ or W₂. However, the incorporation of radially diffuse W 5d orbitals increases the geometric overlap between the respective Mo and W dₓ² and dₓz, dᵧz orbitals which form heterometallic σ- and π-bonds. The result is a metal−metal bond force constant which is slightly higher for MoW than Mo₂, but still weaker than the average of Mo₂ and W₂. We now propose that the unbridged heteronuclear MoW quadruple bond does not exhibit bonding which may simply be described as an average of that observed in the homodimers. Our results indicate that heteronuclear metal−metal bonds are slightly weaker than the average of the homodimers due to a decrease in effective orbital mixing resulting from the difference in constituent atomic orbital energies.

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Supporting Information Available: Complete 2D NOESY/EXCHSY spectrum, calculated and experimental mass spectra for (OEP)MoW(OEP)PF₆ and (TOEP)MoW(TOEP), and normal coordinate analyses for M₂(porphyrin)₂ dimers (56 pages). See any current masthead page for ordering information and Web access instructions.