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Exchange Coupling in Metallocene Trihydride Complexes

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Abstract: The ^1H NMR spectra of the metallocene trihydride complexes $[(\eta\text{-}C_5H_5)_2MH_3]^{n+}$ (M = Mo, W, n = 1; M = Nb, Ta, n = 0) have been investigated as a function of temperature. With the exception of M = Mo, all the complexes exhibit hydride resonances at ambient temperature which are consistent with an AB_2 spin system, with moderate values of J_{A-B} (7-20 Hz). For M = Nb, a novel temperature dependence of J_{A-B} was observed. The observed coupling decreases with decreasing temperature, becoming unresolvable at 243 K, and then reappears at 173 K. The observed coupling is attributed to a magnetic component and a quantum mechanical exchange component, which have opposite signs. The sign of the magnetic coupling is negative. For M = Mo, a single resonance was observed in the hydride region of the ^1H NMR spectrum at room temperature, due to thermally activated A/B site exchange. The static spectrum was obtained at 203 K and reveals an AB_2 spin system with an extremely large value of J_{A-B} (ca. 1000 Hz). This coupling is also temperature dependent, decreasing to 450 Hz at 153 K.

Introduction

We have recently proposed the existence of a quantum mechanical exchange coupling between the hydrogen nuclei in certain transition-metal polyhydride complexes.[1-3] While such couplings are well-known for electrons as demonstrated by the ESR spectra of certain biradicals,[4] the only precedent for such interactions between heavy particles is provided by studies of ^3He at cryogenic temperatures.[5] In contrast, molecular polyhydrides have now been shown to demonstrate substantial exchange couplings between hydrogen nuclei in fluid solution at ambient temperature. The magnitude of these couplings is quite variable, depending on the metal and the nature of the coligands. The occurrence of exchange coupling can in some cases lead to observed proton-proton couplings that are considerably larger than magnetic couplings arising by the normal Fermi contact mechanism. Couplings of up to 1565 Hz have been observed in an iridium complex, with the magnitude of the observed coupling shown to be a sensitive function of the ancillary ligands and of the observation temperature.[2]

A model quantitatively describing this coupling has been previously reported.[2,3] In brief, the observed coupling is found to depend on the distance between the adjacent hydrides and on the vibrational potential that the hydride ligands experience. Since the observable coupling J_{obs} is a combination of the exchange and magnetic contributions[3] given by $J_{obs} = -2J_{ex} + J_m$, a very interesting situation arises when these two components of the observed coupling are comparable in magnitude. While theory predicts that the sign of the exchange coupling J_{ex} is negative,[2,3] leading to an overall positive contribution to the coupling, little information is available regarding the sign of the magnetic coupling in transition-metal hydrides.[6] If the sign of the magnetic coupling is negative, it may cancel out the positive term due to the exchange coupling, and it is in principle possible to have no observable coupling between two protons in a metal polyhydride. Since the exchange coupling component is temperature dependent, this situation would be indicated by a temperature-dependent J_{obs}, which would decrease with decreasing temperature, go through zero, and then increase again as the temperature is lowered further. This paper reports the observation of such behavior in the case of $(\eta\text{-}C_5H_5)_2NbH_3$.

Table I. Coupling Constant as a Function of Temperature for $(\eta\text{-}C_5H_5)_2NbH_3$ (1) in Methylcyclohexane-d_{14}

T, K	J_{obs}	J_{ex}	J_m
303	20.4	13.2	6
293	13.6	9.8	6
283	11.0	8.5	6
273	9.8	7.9	6
263	7.1	6.6	6
253	4.5	5.3	6
243	n.r.[a]	~3	6
173	4	0	6

[a] At this temperature, no coupling was resolved, although a coupling of 2-3 Hz would have been expected. The line width was 9 Hz.

Table II. Coupling Constant as a Function of Temperature for $(\eta\text{-}C_5H_5)_2NbH_3$ (1) in $CDFCl_2$

T, K	J_{obs}	J_{ex}	J_m
263	n.r.[a]	~3	6
243	3.4	1.3	6
193	5.9	0	6
183	6.0	0	6
173	6.0	0	6

[a] At this temperature, no coupling was resolved, although a coupling of ca. 2 Hz would have been expected. The line width was 7 Hz.

Investigations of the metallocene trihydride complexes of tantalum, molybdenum, and tungsten have also been carried out. It is found that the magnitude of the observed exchange coupling is extremely variable, with very large values observed for $(\eta\text{-}C_5H_5)_2MoH_3^+$, while no exchange coupling was found for the tungsten or tantalum analogues.

Results

The anomalous ^1H NMR spectra of the hydride protons in $(\eta\text{-}C_5H_5)_2NbH_3$ (1) has been previously reported by Curtis and co-workers,[9] who reported that the hydride signals corresponded to an AB_2 spin system, with temperature-dependent values of J_{A-B}, ranging from 11 Hz at 301 K down to 0 Hz at 232 K. It was also reported that the observed spectra were field dependent and that the line width of the signal due to H_A was considerably greater than that due to H_B.

We find, in accord with the results of Curtis and co-workers, that the hydride region of the ^1H NMR spectrum of **1** at room temperature (methylcyclohexane-d_{14}) consists of a poorly resolved

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[6] A coupling $J_{H-H} = -14$ Hz has been reported for $H_2Ru[P(OMe)_3]_4$.[7] A negative sign for J_{H-H} has been inferred for a rhodium dihydride from a polarization transfer experiment.[8]

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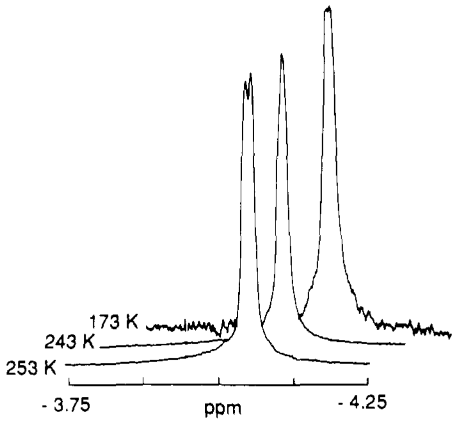

Figure 1. Partial ^{1}H NMR spectra of (η-C_5H_5)$_2$NbH$_3$ (methylcyclohexane-d_{14}, 490 MHz) at various temperatures.

triplet (1 H) at δ −3.20 ppm and a doublet (2 H) at δ −4.05 ppm, consistent with the spin system description AB_2 or AX_2. The coupling J_{A-B} at 303 K is 20.4 Hz, as measured by the peak separation in the doublet resonance. The coupling shows a striking temperature dependence, decreasing rapidly as the temperature is lowered and becoming undetectable at 243 K.[10] Upon further cooling, the spectrum remains essentially unchanged down to 173 K, where the coupling *reappears*. The coupling J_{A-B} at 173 K is 4 Hz (see Figure 1 and Table I).

Better resolution of the low-temperature spectra was achieved with CDFCl$_2$ as solvent for complex **1**. The measured couplings differ significantly from those obtained in methylcyclohexane (see Table II).

In contrast to the niobium complex **1**, we find that the ^{1}H NMR spectrum of the tantalum analogue (η-C_5H_5)$_2$TaH$_3$ is independent of temperature in the range 203–303 K, with coupling between the hydride protons of J_{A-B} = 9.5 Hz.

Consistent with the initial report by Wilkinson and co-workers in 1961, we have found that the ^{1}H NMR spectrum of the tungsten complex in the hydride region consists of an AB_2 spin system, with J_{A-B} = 8.5 Hz.[12] The observed coupling is temperature independent in the range 203–303 K. In contrast, the room temperature ^{1}H NMR spectrum of the molybdenum analogue exhibits a single resonance in the hydride region at δ −6.15 ppm (CD_2Cl_2), again consistent with the previous report.[12] We have found that on cooling the sample to 243 K, two additional broad resonances appear flanking the central line. Further cooling to 203 K gives a static sharp line spectrum consisting of three resonances in the intensity ratio 1:10:1. The spectrum at 203 K can be fit computationally with parameters δ_A = −6.02 ppm, δ_B = −6.25 ppm, and J_{A-B} = 1000 Hz (490 MHz). On lowering the temperature to 153 K (CDFCl$_2$ solvent, 490 MHz), the coupling is reduced sufficiently to allow the resolution of additional detail and the spectrum can be fit definitively to a J_{A-B} value of 450 Hz (see Figure 2).

Discussion

The temperature-dependent couplings between the hydride protons of **1** are readily explicable in terms of exchange coupling between the hydridic protons. As noted above, there are two distinct components of the observed coupling J_{A-B} or J_{obs}, which are due to the magnetic and exchange contributions. The magnetic component (J_m) is the result of coupling mediated by the conventional Fermi contact mechanism and is expected to be independent of temperature. The exchange coupling term (J_{ex}), due to quantum mechanical effects, is mediated through the vibrational potentials and is dependent on temperature. Pervious observations have demonstrated that exchange coupling increases exponentially with increasing temperature in all known examples.[3] As noted above, the observed coupling is given by $J_{obs} = -2J_{ex} + J_m$. Previous cases that have been studied have generally exhibited quite large exchange couplings which dwarf the relatively small contribution of the magnetic coupling. In the case of complex **1**, the exchange coupling contribution and the magnetic coupling are of similar magnitude (see Table I). Thus the observed coupling J_{obs} decreases with decreasing temperature, becoming undetectable at 243 K. There are two possible explanations for this behavior. It is possible that J_m = 0 for complex **1**. Alternatively, if $J_m \neq 0$ the sign of J_m is required to be negative. The former possibility is ruled out by the data obtained at 173 K, where the coupling *reappears* (see Figure 1). Although the resolution is poor, an approximate value for J_{obs} of 4 Hz was obtained at 173 K. Thus the observed coupling decreases with temperature and apparently goes to zero and then reappears at still lower temperatures, due entirely to the temperature dependence of the exchange coupling component. Assuming that the value of J_{obs} obtained at 173 K reflects a situation where J_{ex} has been reduced to zero or near zero, then a value of J_m of approximately 4 Hz is indicated. If this assumption is correct, the value of J_{obs} should be constant at still lower temperatures. Alternatively, if J_{ex} is still decreasing at 173 K, then J_m may be somewhat greater than the estimated value of 4 Hz. Unfortunately, lower temperature data could not be obtained in this experiment due to the low solubility of **1** and the freezing of the solvent. (In fact, data obtained in a freon solvent presented below are consistent with a J_m of 6 Hz.)

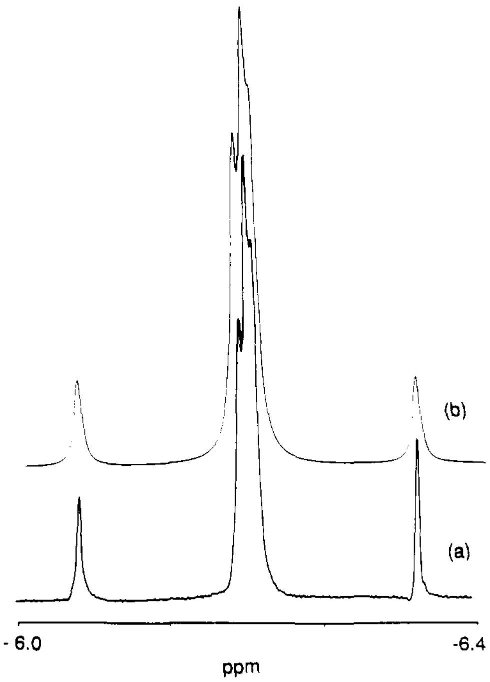

Figure 2. (a) Partial ^{1}H NMR spectra of [(η-C_5H_5)$_2$MoH$_3$]BF$_4$ (CDFCl$_2$, 490 MHz, 153 K). To facilitate visual comparison with calculated spectra, the data were processed by using resolution enhancement with lorentzian line broadening of −2 Hz and gaussian broadening of 0.2 Hz. The natural line width in the absence of resolution enhancement is ca. 3 Hz. (b) Spectrum calculated for ν_A = −6.05 ppm, ν_B = −6.27 ppm, and J_{A-B} = 450 Hz.

A similar temperature dependence has been reported for the related niobium complexes (η-$C_5H_{5-n}R_n$)$_2$NbH$_3$ (R = SiMe$_3$; n = 1, 2).[13] In these complexes, J_{obs} varies with increasing temperature from 0 to 90 Hz. These observations have also been interpreted in terms of the operation of exchange coupling.[3] In

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(10) The observed coupling constants reported here differ very slightly from those reported by Curtis and co-workers.[9] We attribute these differences to minor errors in calibration of probe temperatures. All temperatures reported here were carefully calibrated by comparison to the chemical shift differences in the spectrum of pure methanol.[11]

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this case, the exchange coupling is much larger than the magnetic coupling. Extremely low temperature data are not available for these complexes. Presumably the coupling will reappear at lower temperature in these complexes, but sufficiently low temperatures may not be accessible. In contrast to the effect of $SiMe_3$ substituents on the cyclopentadienyl rings, permethylation leads to very small couplings. Thus it has been reported that the hydride region of the ^1H NMR spectrum of $(\eta-C_5Me_5)_2NbH_3$ consists of an AX_2 spin system with $J_{H-H} = 4$ Hz.[14] This modest observed coupling may indicate that there is no exchange coupling, but the occurrence of a small exchange coupling (less than 5 Hz) cannot be ruled out in the absence of variable-temperature data. The effect of permethylation is consistent with our previous work[2] on iridium complexes where the magnitude of the exchange coupling was found to be inversely proportional to the electron density at the metal.

The deduction of a negative sign for the two-bond H–H coupling in **1** is consistent with limited literature data for such couplings, which have also reported a negative sign.[6] This may be a general observation for metal hydrides. It should be pointed out that experiments of the type reported here are also in principle capable of detecting a positive magnetic coupling. This situation would be indicated by a decrease in J_{obs} with decreasing temperature, asymptotically approaching a constant, temperature-independent value equal to J_m.

To obtain more definitive low-temperature data for **1**, the freon solvent $CDFCl_2$ was employed. Complex **1** reacts slowly with this solvent at ambient temperature, but solutions are indefinitely stable at low temperatures. The data (see Table II) reveal that the values of J_{obs} obtained are quite different from those obtained in methylcyclohexane at the same temperatures. In this solvent, the coupling is not observable at 263 K, and then *increases* to 3.5 Hz at 243 K. The values for J_{obs} continue to increase as the temperature is lowered, ultimately reaching a constant value of 6 Hz. These data are only interpretable in terms of a remarkable solvent effect on the value of J_{ex}. For example, at 263 K, the value for J_{ex} in methylcyclohexane is 6.6 Hz. At the same temperature, the value of J_{ex} in $CDFCl_2$ is ca. 3 Hz. This reduction of the exchange coupling in the freon solvent has the effect of moving to higher temperatures the point at which no coupling is observable, and the two components of the coupling cancel. While the origin of this effect is no doubt differential solvation of **1** in the two solvents, it is somewhat surprising that the effect is so large.

These observations clearly establish that values for two-bond H–H couplings in metal polyhydrides reported at a single temperature cannot be regarded as due solely to normal magnetic couplings. The situation reported here for **1** in which the exchange contribution to the coupling is comparable in magnitude to the magnetic coupling may in fact occur widely and will be indicated by temperature-dependent values for J_{obs}.

In contrast to the niobium complex **1**, we find that the ^1H NMR spectrum of the tantalum analogue $(\eta-C_5H_5)_2TaH_3$ is independent of temperature over a wide range of temperatures, with coupling between the hydride protons of $J_{A-B} = 9.5$ Hz. This indicates that there is no significant exchange coupling in this complex. Since it is known that the magnitude of exchange coupling in polyhydride complexes is a very sensitive function of the proton–proton distance,[2,3] this may indicate that the H–H distance is slightly greater in the tantalum complex. Structural data of sufficient precision (neutron diffraction) are only available for the tantalum complex,[15] although X-ray diffraction results indicate that the niobium and tantalum complexes have very similar structures.[15] Previous studies have also established that the magnitude of proton–proton exchange coupling is critically dependent on the nature of the vibrational potential experienced by the hydride ligands.[2,3] The observed difference between the niobium and tantalum complexes may be attributable to this factor. Qualitatively, this explanation would require that the Ta–H bonds are slightly "stiffer" than those found in **1**.

Since our earlier studies of iridium complexes revealed large exchange couplings only in cationic species, an examination of the cationic analogues $[(\eta-C_5H_5)_2MH_3]^+$ (M = Mo, W) was undertaken. These molecules were originally prepared and studied by Wilkinson and co-workers in 1961.[12] Consistent with the earlier data, we have found that the ^1H NMR spectrum of the tungsten complex in the hydride region consists of an AB_2 spin system (with appropriate satellite resonances due to coupling to ^{183}W), with $J_{A-B} = 8.5$ Hz.[12] The observed coupling is temperature independent in the range 203–303 K. Thus the cationic tungsten complex displays very similar NMR behavior to that noted above for the neutral tantalum analogue.

In contrast, the room temperature ^1H NMR spectrum of the molybdenum analogue $[(\eta-C_5H_5)_2MoH_3]^+$ exhibits a single resonance in the hydride region at δ −6.15 ppm (CD_2Cl_2), again consistent with the previous report.[12] The variable-temperature ^1H NMR spectrum of this cation has not previously been studied. We have found that on cooling the sample to 243 K, two additional broad resonances appear flanking the central line. These observations are consistent with a highly second order AB_2 spin system undergoing thermally activated A/B site exchange. Further cooling to 203 K diminishes the rate of site exchange, leading to a static sharp line spectrum consisting of three resonances in the intensity ratio 1:10:1. The spectrum at 203 K can be fit computationally with parameters $\delta_A = -6.02$ ppm, $\delta_B = -6.25$ ppm, and $J_{A-B} = 1000$ Hz (490 MHz). This value of the coupling represents a minimum value, since the input of higher values into the simulation calculation gives the same limiting spectrum. For an AB_2 spin system under highly second order conditions ($J_{A-B} > 10\ \Delta\delta$), the spectrum consists of three resonances in the intensity ratio 1:10:1, since the intensity of the weak outer lines has been reduced to near-zero. Further increases in the J_{A-B} value do not affect the appearance of the spectrum. From such spectra, the values for the chemical shifts can be accurately fit, but only a *minimum* value for J_{A-B} can be determined. A similar situation was previously reported in the case of the neutral ruthenium trihydride complex $(\eta-C_5H_5)Ru(PPh_3)H_3$.[16]

On lowering the temperature to 153 K ($CDFCl_2$ solvent, 490 MHz), the coupling is reduced sufficiently to allow the resolution of additional detail and the spectrum can be fit definitively to a J_{A-B} value of 450 Hz (see Figure 2). In this case, five of the eight resonances expected for the AB_2 spin system are resolvable, but the three weak outer lines could not be detected.

These extremely large couplings are comparable to those that we have previously observed in cationic iridium complexes[2] and are attributed to a large exchange coupling which in this case dwarfs the magnetic coupling. The striking difference between the cationic molybdenum complex and the neutral niobium analogue is consistent with previous observations on iridium complexes in which it was noted that the exchange coupling is inversely proportional to the electron density at the metal center. The contrast between the large exchange coupling observed in the molybdenum complex versus no exchange coupling for the tungsten analogue is quite remarkable. As noted above for the comparison of Nb and Ta analogues, these two complexes are presumably very similar structurally, so significant differences in the H–H distances between the hydride ligands would not be expected. Recall that in the case of Nb, the exchange coupling is modest in magnitude. For Ta, no exchange coupling was observed. Much larger differences are exhibited between the cationic Mo and W complexes. The large difference in the magnitude of the exchange couplings presumably reflects a significant difference in the vibrational potential experienced by the hydride ligands. Such a difference would presumably be reflected by changes in the frequency of the M–H bending modes in the infrared or Raman spectra of these complexes. While such modes have not been observed, a recent

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study by Perutz and co-workers[17] notes that the M-H bending modes for the *neutral* analogues show the expected trend in that the Mo complex $(\eta\text{-}C_5H_5)_2MoH_2$ exhibits a M-H bending mode ca. 60 cm^{-1} lower in frequency than that of $(\eta\text{-}C_5H_5)_2WH_2$. It is not unreasonable to attribute the large differences in coupling observed in the Mo and W systems to relatively subtle changes in the M-H bending modes, which are indicative of the vibrational potentials experienced by the hydride ligands. Our previous work on quantitative models for exchange coupling predicted that a decrease in the M-H bending frequency of 100 cm^{-1} would reduce the exchange coupling by two orders of magnitude.[3] While the comparison of known bending frequencies of the neutral molecules is not strictly valid for the cationic trihydride complexes considered here, it is reasonable to expect that a similar trend may also hold for the cations.

In conclusion, it is clear that exchange coupling is an important factor in understanding the ^1H NMR spectra of certain metallocene trihydride complexes. In general, "normal" values (<20 Hz) for two-bond H-M-H couplings observed in some polyhydride complexes may not be entirely due to magnetic couplings. Further examination of such complexes may reveal a temperature dependence of the coupling due to an exchange coupling component. In addition, this work has shown that the sign of the two-bond magnetic coupling between hydride ligands attached to a metal is negative in the case of $(\eta\text{-}C_5H_5)_2NbH_3$. This conclusion is consistent with the very limited data available for such couplings in the literature and may be a general observation. Further work is in progress to investigate these possibilities.

Experimental Section

All manipulations were conducted under dry nitrogen following standard Schlenk techniques or in a drybox. $(\eta\text{-}C_5H_5)_2NbH_3$ was prepared from $(\eta\text{-}C_5H_5)_2NbCl_2$ by the method of Curtis and co-workers.[9] $(\eta\text{-}C_5H_5)_2TaH_3$[18] and $(\eta\text{-}C_5H_5)_2MoCl_2$[19] were prepared according to Green and co-workers. Proton NMR spectra were recorded on a modified Bruker instrument at 490 MHz. Probe temperatures were calibrated by comparison to the observed chemical shift differences in the spectrum of pure methanol with use of the data reported by Van Geet.[11] Temperatures below the freezing point of methanol were obtained by extrapolation.

Preparation of $(\eta\text{-}C_5H_5)_2MoH_2$. The procedure of Dias and Ramão was followed, with some modification.[20] To a suspension of $(\eta\text{-}C_5H_5)_2MoCl_2$ (297 mg, 1 mmol) in 30 mL of 1,2-dimethoxyethane (DME) was added an excess of $NaBH_4$ (380 mg, 10 mmol). After 18 h of stirring at room temperature, the yellow brown solution was taken to dryness. Sublimation (75 °C, 10^{-3} mmHg) affords the product as bright yellow crystals (200 mg, 90%).

Preparation of $[(\eta\text{-}C_5H_5)_2MoH_3]BH_4$. $(\eta\text{-}C_5H_5)_2MoH_2$ (100 mg) was dissolved in 25 mL of Et_2O. Excess 85% $HBF_4{\cdot}Et_2O$ was added, affording a flocculent white precipitate of $[(\eta\text{-}C_5H_5)_2MoH_3]BF_4$, which was collected by filtration. A similar procedure was employed to prepare $[(\eta\text{-}C_5H_5)_2WH_3]BF_4$. The precursor $(\eta\text{-}C_5H_5)_2WH_2$ was the generous gift of Professor J. R. Norton.

Acknowledgment. This work was supported by the National Science Foundation. We thank Professor J. R. Norton for a generous gift of $(\eta\text{-}C_5H_5)_2WH_2$.

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Structure of a Carbon Monoxide Adduct of a "Capped" Porphyrin: Fe(C_2-Cap)(CO)(1-methylimidazole)

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Abstract: The structure of Fe(C_2-Cap)(CO)(1-MeIm) has been determined by single-crystal X-ray diffraction methods. It consists of the packing of two crystallographically independent porphyrin molecules and solvate molecules. Both porphyrin molecules display the expected connectivity in which the benzene caps are slanted with respect to the mean porphyrin planes (dihedral angles of 15.5 and 11.5° for molecules 1 and 2, respectively). The centroids of the cap atoms are 5.57 and 5.68 Å from the mean porphyrin planes. Since this distance is 3.96 Å in H_2(C_2-Cap), the cap moves 1.6-1.7 Å further away from the porphyrin upon binding a CO ligand inside the cavity. The coordinated CO ligand is slightly but detectably distorted from linearity, being both bent and tilted off the axis normal to the porphyrin. The Fe-C-O bond angle and the off-axis displacements for the C and O atoms of CO are 173.1 (9)°, 0.17 Å, and 0.41 Å, respectively, for molecule 1, and 175.8 (8)° and 0.12 and 0.28 Å, respectively, for molecule 2. Crystallographic data: triclinic $P\bar{1}$, $Z = 4$, $a = 18.022$ (2) Å, $b = 20.017$ (1) Å, $c = 20.691$ (2) Å, $\alpha = 70.507$ (7)°, $\beta = 76.232$ (10)°, $\gamma = 82.549$ (7)° at -150 °C, 18468 observations, 1740 variables, $R(F) = 0.096$ ($F_o^2 > 3\sigma(F_o^2)$).

Introduction

Modeling of oxygen-binding heme proteins has been an active field of research in the last two decades.[1] Numerous model systems have been synthesized, and their affinities for axial bases and small molecules have been measured.[1] Many such model systems have contributed markedly to our understanding of structure-function relationships of natural systems, especially to current ideas about O_2/CO discrimination.[2] Recent attention has focused on the distorted geometry of the bound CO ligand

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[†] Pohang Institute of Science and Technology.

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