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Structure-Sensitive Resonance Raman Bands of Tetraphenyl and "Picket Fence" Porphyrin–Iron Complexes, Including an Oxyhemoglobin Analogue

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Abstract: Resonance Raman spectra are reported for iron *meso*-tetraphenylporphine (TPP) and *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-o-pivaloylamidophenyl)porphine ($T_{piv}PP$), in 2+ and 3+ oxidation states and in high, low, and intermediate (Fe^{2+}) spin states. Non-totally symmetric modes are seen weakly, or are absent, and only polarized modes can be monitored through the series of complexes. Three of these, $\sim$390, $\sim$1360, and $\sim$1560 cm^{-1}, show appreciable frequency shifts associated with oxidation and spin-state changes. The vibrational signature of the five-coordinate (high-spin) Fe^{2+} complexes is particularly distinct. The $Fe-O_2$ stretching mode of $Fe(T_{piv}PP)(1-MeIm)O_2$ is located at 568 cm^{-1} (confirmed utilizing $^{18}O_2$), very close to its value in oxyhemoglobin (567 cm^{-1}). This relatively high frequency is consistent with appreciable multiple bond character for the $Fe-O_2$ bond.

Introduction

In systematic studies of metalloporphyrin chemistry, *meso*-tetraphenylporphine (TPP) is frequently the molecule of choice because of its convenient synthesis. Although the pattern of peripheral substitution (see Figure 1, ref 6a) is very different from that of physiological porphyrins, extensive comparison of crystal structure determinations suggests that the bonding within the porphinato core is essentially the same in both porphyrin classes.[2a] Recently, the TPP framework has been used to erect a "picket fence", in the form of pivaloylamide groups substituted at the *o*-phenyl positions, with the aim of providing a protected coordination environment.[2b] This approach led to the preparation of the first (and so far only) isolable, crystalline dioxygen complex of an iron porphyrin.[3] Its crystal structure reveals the Fe–O–O unit to be bent, as in the Pauling model for oxyhemoglobin.

Resonance Raman (RR) spectroscopy has been extensively applied to heme proteins[4] and metalloporphyrin[5] analogues. Vibrational modes of the porphyrin ring can be monitored with high sensitivity, and are observed to shift frequency in a characteristic manner[4] which is associated with the oxidation state or axial ligation of the central metal atom. Protein influence on porphyrin structure can be evaluated from the vibrational pattern. Tetraphenylporphyrins give RR spectra that are quite different in appearance from those of physiological porphyrins, and while numerous TPP spectra have been reported,[6] no structural interpretations have been offered.

We have examined the vibrational patterns of a series of iron TPP complexes, several of whose crystal structures are available, and of a corresponding series of $T_{piv}PP$ [*meso*-tetra($\alpha,\alpha,\alpha,\alpha$-o-pivaloylamidophenyl)porphine] complexes. While the structural utility of the data is more limited than for the physiological porphyrins, three structure-sensitive bands are identified. The vibrational pattern for five-coordinate (high-spin) iron(II) derivatives is particularly distinct. The iron–oxygen stretching mode of the "picket fence" dioxygen complex has been identified at 568 cm^{-1}. Its frequency is close to that observed for oxyhemoglobin (567 cm^{-1})[7] and establishes the similarity of the iron–oxygen bond in protein and analogue. The relatively high frequency is consistent with substantial multiple bond character.

Experimental Section

meso-Tetraphenylporphine was purchased from Aldrich Chemical Co., Inc. Treatment with 2,3-dichloro-5,6-dicyanobenzoquinone and chromatography on alumina (Fisher A-540) removed all traces of tetraphenylchorin.[8] The iron(III) complexes and β carbon deuterated species were prepared as indicated previously.[6a] The synthesis of *meso*-tetra($\alpha,\alpha,\alpha,\alpha$-o-pivaloylamidophenyl)porphineiron(III) bromide has been described.[2] The iron(II) complexes were prepared in situ by reduction of a methylene chloride solution of the iron(III) complex with aqueous sodium dithionite.[5a]

The bisimidazole (1m), 1-methylimidazole (1-MeIm), and 2-methylimidazole (2-MeIm) iron(II) (TPP) and $T_{piv}PP$ derivatives gave resonance Raman spectra which indicated the presence of ad-

Table I. Resonance Raman Frequencies (cm^{-1}) for TPP and $T_{piv}PP$ Derivatives in CH_2Cl_2 Solution

A. Five-Coordinate Fe(III)

	Fe(TPP)Cl	(d_8)[a]	Fe(T_{piv}PP)Br	Fe(TPP)$_2$O	(d_8)	Fe(T_{piv}PP)$_2$O
(1)[b]	1605 (p)	(1600)	1609 (p)	1599 (p)	(1599)	1605 (p)
(2)			1565 (dp)	1561 (sh) (dp)	(1561)	1565 (sh)
(3)	1555 (p)	(1534)	1556 (p)	1553 (p)	(1532)	1556 (p)
(4)	1510 (vw, ap)		1515 (ap)	1511 (ap)	(1511)	1520 (ap)
(5)				1495 (dp)	(1444)	1496 (vw)
(6)	1454 (p)		1470 (sh, br, dp)	1450 (p)	(1428)	1455 (p)
(7)	1366 (p)	(1353)	1366 (p)	1359 (p)	(1348)	1364 (p)
(8)	1338 (vw, ap)		1334 (ap)	1333 (ap)	(1263)	1336 (ap)
(9)	1270 (sh)	(1270)	1270 (sh)	1271 (sh, dp)	(1263)	1286 (sh, dp)
(10)	1240 (p)	(1237)	1259 (p)	1237 (p)	(1234)	1256 (p)
(11)	1225 (ap)		1224 (ap)	1234 (ap)	(1167)	1238 (ap)
(12)			1205 (w)			1208 (p)
(12a)						1106 (vw)
(13)	1084 (p)	(998)	1080 (p)	1083 (w, p)	(991)	1080 (p) (dp)
(14)				1030 (vw, p)	(1030)	1030 (vw)
(15)			1015 (dp)	1014 (dp)	(877)	
(16)	1009 (p)	(1003)	1001 (p)	1004 (p)	(1005)	1001 (p)
(17)				995 (p)	(991)	
(18)	890 (p)	(890)	895	886 (p)	(886)	890 (p)
(19)				848 (dp)	(851)	
(20)				827 (ap)		
(21)	640 (w)	(638)		640 (p)	(640)	
(22)				400 (br)	(398)	
(23)	390 (p)	(380)	391 (p)	390 (p)	(382)	392 (p)
(24)				363 (p)	(363)	371 (sh, p)
(25)	334 (vvw)	(318)				
(26)	256 (br)			257 (dp)	(257)	241
(27)	202 (br)	(202)	212 (p)	195 (dp)	(195)	
(28)			179 (p)	173	(163)	

B. Six-Coordinate Fe(III)]

	Fe(TPP)(Im)$_2$Cl	(d_8)	Fe(T_{piv}PP)(Im)$_2$Br	Fe(T_{piv}PP)(1-MeIm)-(O$_2$)
(1)	1605 (sh)		1609 (p)	1605
(2)	1582 (sh)(dp)	(1579)		
(3)	1568 (p)	(1541)	1565 (p)	1563
(4)	1540 (vw, ap)	(1541)		
(5)	1505 (dp)		1510 (dp)	1503
(6)	1456 (p)	(1455)	1470 (vw, br, sh)	
(7)	1370 (p)	(1359)	1366 (p)	1366
(8)	1340 (ap, vw)	(1267)	1340 (vvw)	
(9)	1275 (sh, dp)			1280
(10)	1238 (p)	(1234)	1258 (p)	1257
(11)				
(12)			1210 (p)	1208
(12a)			1115 (vvw)	1104
(13)	1084 (p)	(1000)	1085	1078
(14)	1029 (sh, p)		1020 (sh, dp)	
(15)				
(16, 17)	1009 (p)	(1008)	1005	1003
(18)	890	(890)	895	889
(19)				
(20)				
(21)	643	(643)		642
(22)	398 (sh)	(400)		(568ν_{Fe-O_2})
(23)	390 (p)	(383)	390 (p)	384
(24)				
(25)	336 (vw)	(325)		
(26)	232	(230)		
(27)	204			
(28)				

C. Four- and Five-Coordinate Fe(II)

	Fe^{II}TPP	Fe^{II}(T_{piv}PP)	Fe(TPP)(2-MeIm)	(d_8)	Fe(T_{piv}PP)(2-MeIm)
(1)	1603 (p)	1608	1598	(1596)	1606
(2)					
(3)	1565	1566	1537	(1516)	1540
(4)					
(5)	1505 (w)		1484		1488 (w, dp)
(6)			1451 (w)	(1445)	
(7)	1370	1370	1342	(1337)	1344
(8)					
(9)		1280 (sh)		(1266)	1275 (sh)
(10)	1240	1259	1229	(1227)	1252
(11)					
(12)		1209			1204
(12a)		1110			1105

Table I (*Continued*)

	Fe^{II}TPP	Fe^{II}(T$_{piv}$PP)	Fe(TPP)(2-MeIm)	(d_8)	Fe(T$_{piv}$PP)(2-MeIm)
(13)	1082	1080	1074	(993)	1074
(14)			1032		
(15)					
(16)	1005 (br)	996	1004	(1002)	995
(17)		996	990		995
(18)			884	(891)	890
(19)					
(20)					
(21)			640	(640)	640
(22)			424		
(23)	392 (br)	372	372	(363)	366
(24)					
(25)			337		
(26)			232 (sh)		261
(27)			204	(204)	209
(28)					158 (br)

D. Six-Coordinate Fe(II)

	Fe(TPP)(1-MeIm)$_2$	Fe(T$_{piv}$PP)(Im)$_2$	Fe(TPP)(pip)$_2$[c]	Fe(TPP)(py)$_2$[d]	Fe(TPP)(γ-pic)$_2$[e]	Fe(T$_{piv}$PP)(py)$_2$[d]	Fe(T$_{piv}$PP(1-MeIm)$_2$
(1)	1599	1607			1603	1605	1605
(2)							
(3)	1557	1558	1561	1558	1558	1560	1560
(4)			1540 (ap)				
(5)	1475	1490 (w, br)		1484 (dp)	1486	1480 (w, dp)	
(6)							
(7)	1354	1356	1356	1360	1360	1360	1355
(8)							
(9)	1272	1275		1265 (w)	1270 (w)		
(10)	1227	1255	1230 (p)	1232	1236	1255	1253
(11)			1230 (ap)				
(12)		1205					1202
(12a)		1105					1106
(13)	1073	1080		1076	1078	1080	1076
(14)	1031			1030	1030	1030	
(15)							
(16, 17)	1000	996		995	995	998	995
(18)				885	886		889
(21)			638	638	642		642
(22)							
(23)	382	382	387	388	388	382	384
(24)							
(25)	337 (vvw)		336	337	338		
(26)							
(27)	201			204	204		
(28)							

[a] (d_8) Frequencies in parentheses are for the preceding complex deuterated at the β-pyrrole positions. [b] Tentative mode assignments (see ref 6a) are as follows (symmetry designations A$_1$, B (= B$_1$ or B$_2$), A$_2$; see Figure 1 of ref 6a for atom labeling): (1) A$_1$, phenyl; (2) B, $\nu_{C_\alpha-C_m}$; (3) A$_1$, $\nu_{C_\beta-C_\beta}$; (4) A$_2$, $\nu_{C_\alpha-C_m}$; (5) B, $\nu_{C_\beta-C_\beta}$; (6) A$_1$, $\nu_{C_\alpha-C_\beta}$; (7) A$_1$, $\nu_{C_\alpha-C_N}$; (8) A$_2$, $\nu_{C_\alpha-C_\beta}$ + $\delta_{C_\beta-H}$; (9) B, $\nu_{C_\alpha-N}$; (10) A$_1$, ν_{C_m-Ph}; (11) A$_2$, $\nu_{C_\alpha-N}$ + $\delta_{C_\beta-H}$; (12) phenyl; (13) A$_1$, B $\delta_{C_\beta-H}$; (14) A$_1$, $\delta_{C_{Ph}-H}$; (15) B, $\delta_{C_\beta-H}$; (16) A$_1$, $\nu_{C_\alpha-C_m}$; (17), (18), phenyl; (21) porphyrin deformation; (23) A$_1$, porphyrin deformation; (24) A$_1$, $\nu_{Fe-O-Fe}$ (dimers). [c] From ref 6c. [d] Bound pyridine modes[5a] observed at 1601, 1215, 1046, 1010, 634, and 179 cm^{-1}. [e] Bound picoline modes[5a] observed at 1617, 1209, 1063, 1025, 817, 543, and 162 cm^{-1}.

ditional minor species in solution. This is in disagreement with the binding constant measurements of Brault and Rougee[9] in which only one species was seen to predominate in solution containing excess axial ligand. Our results may reflect partitioning of the ligand between the aqueous and CH$_2$Cl$_2$ layers. The spectral interpretations are unaffected by this complication.

To prepare the O$_2$ adduct of Fe(T$_{piv}$PP)(1-MeIm), a CHCl$_2$ solution of Fe^{III}(T$_{piv}$PP)Br ($\sim$1 mM) and 1-MeIm ($\sim$4 mM) was degassed with argon and reduced with aqueous sodium dithionite. The CH$_2$Cl$_2$ layer was then transferred under argon into a stoppered spinning cell. Oxygen was added by allowing a stream of oxygen to flow over the solution in the spinning cell for $\sim$10 s. Reversibility of adduct formation was checked by degassing with argon.

To prepare the ^{18}O$_2$ analogue, the CH$_2$Cl$_2$ solution of reduced heme was transferred under argon to a specially constructed spinning cell fitted with two vacuum tight rubber septums. A slight evacuation of

the cell was followed by exposure to ^{18}O$_2$ (1 atm) utilizing 20 gauge needle connections. Subsequent exchange with ^{16}O$_2$ was accomplished by flowing O$_2$ through the unstoppered cell and resealing.

The methylene chloride was obtained from Burdick and Jackson Laboratories. Pyridine and γ-picoline were distilled and stored in the dark over molecular sieves. 1-Methylimidazole was distilled before use. Imidazole and 2-methylimidazole were recrystallized from benzene.

Spectra were obtained as reported previously.[6a] Laser power levels were 100-300 mW, and the spectral band-pass was 5 cm^{-1}. Most spectra were recorded with 4579-Å excitation, but the location of non-totally symmetric modes was checked with longer wavelengths.

Results and Discussion

Figure 1 shows RR spectra for several iron T$_{piv}$PP deriva-

Figure 1. Resonance Raman spectra of Fe(T_{piv}PP) derivatives with 457.9-nm excitation. Concentration: 1 mg/mL.

Table II. Structure-Sensitive Bands of Iron TPP and T_{piv}PP Complexes[a]

	A	B	C
Fe(III) h.s.[b]	1555	1366	390
Fe(III) l.s.[c]	1568	1370	390
Fe(III) O_2[d]	1563	1366	384
Fe(II) i.s.[e]	1565	1370	392
Fe(II) l.s.[f]	1557	1354	382
Fe(II) h.s.[g]	1537	1342	372

[a] Frequencies in cm^{-1}; all three bands are polarized. [b] High-spin Fe(III): Fe(TPP)Cl, Fe(T_{piv}PP)Br, and the μ-oxo dimers. [c] Low-spin Fe(III): bisimidazole adducts. [d] Fe(T_{piv}PP)(1-MeIm)O_2. [e] Intermediate-spin: four-coordinate FeTPP and FeT$_{piv}$PP. [f] Low-spin Fe(II): bisimidazole adducts. [g] High-spin Fe(II): 2-methylimidazole adducts.

spectra are dominated by polarized (totally symmetric) modes, even upon excitation in the visible absorption bands, where the spectra of the physiological porphyrins are dominated by non-totally symmetric modes. The latter are much weaker in TPP complexes, relative to the symmetric modes, and are frequently unobservable.

The vibrational frequencies of T_{piv}PP complexes are very close to those of the corresponding TPP complexes, except for modes assigned to the phenyl groups, which are expected to be perturbed by the pivaloylamide substitution. In addition to phenyl modes near 1605, 1030, 995, and 886 cm^{-1} which are also seen in TPP spectra,[6a] the T_{piv}PP spectra show a band at ~1210 cm^{-1} which is characteristic of ortho-disubstituted benzenes.[10] The spectra of iron(II) bispyridine (or bis-γ-picoline) complexes of both TPP and T_{piv}PP show bound pyridine (or γ-picoline) modes, presumably enhanced via resonance with a Fe(II) $\rightarrow$ pyridine charge transfer. They occur at essentially the same frequencies, as observed for the corresponding mesoporphyrin IX complexes.[5a]

A. Structure-Sensitive Bands. For physiological hemes, five bands have been identified whose frequences are sensitive to oxidation state and axial ligation (spin state) or both.[4a] These follow: I, ~1366 cm^{-1} (p); II, ~1500 cm^{-1} (p); III, ~1550 cm^{-1} (dp); IV, ~1580 cm^{-1} (ap); V, ~1630 cm^{-1} (dp) (p = polarized, dp = depolarized, ap = anomalously polarized). None of these find counterparts in the TPP spectra except for the ~1360-cm^{-1} band. This is one of the most intense polarized bands for either type of porphyrin, and it probably corresponds approximately to the breathing mode of the pyrrole C–N bonds.[6a,f] For physiological hemes, this is a well-known "oxidation state marker", shifting from ~1370 cm^{-1} in Fe(III)

tives. The RR spectra for the iron TPP derivatives are almost identical with those for iron T_{piv}PP. (See also ref 6a for Fe(TPP) spectra.)

Table I lists the RR frequencies for the complexes included in this study. Tentative assignments are also indicated, based on the study of [Fe(TPP)]$_2$O, reported in the preceding article.[6a] As discussed there, the RR pattern for TPP is quite different from that of physiological porphyrins for the following reasons: (1) the different pattern of peripheral substitution markedly alters the ring–substituent vibrational interactions; (2) several phenyl modes are resonance enhanced; and (3) the

Figure 2. (A) Resonance Raman spectrum of Fe(T_{piv}PP)(1-MeIm)/CH_2Cl_2 with 457.9-nm excitation. Concentration: 1 mg/mL. (B) Same as A, after O_2 addition. (C) Same as B, after flushing with Ar.

hemes to ~1360 cm^{-1} in Fe(II) hemes, although it is sensitive to the extent of π-back-donation from iron to porphyrin as shown by its systematic variation with π-acceptor strength of the axial ligand in a series of Fe(II) mesoporphyrin complexes.[5a] In the TPP and $T_{piv}PP$ spectra, there is likewise a decrease from 1370 to 1354 cm^{-1} on reduction of Fe(III) to Fe(II) in the bisimidazole complexes. There is also some sensitivity to Fe(II) axial ligand π acidity, as shown by the increase from 1354 to 1360 cm^{-1} on going from imidazole to pyridine, and to 1366 cm^{-1} when O_2 is the axial ligand (see Figure 2).

For physiological hemes, band I is insensitive to spin state, but in the TPP spectra, an appreciable spin-state sensitivity is apparent. Thus, the high-spin Fe(III) frequencies (chlorides, bromides, and μ-oxo dimers) cluster around 1364 cm^{-1}, ~6 cm^{-1} below the low-spin frequencies, while the frequencies for high-spin Fe(II) (2-methylimidazole complexes) are 1342 and 1344 cm^{-1} for TPP and $T_{piv}PP$, respectively, ~12 cm^{-1} below the low-spin (bisimidazole) values. These decrements, although not as pronounced, are similar to those found for bands II, IV, and V for physiological hemes, the Fe(II) decrease being substantially larger than the Fe(III) decrease. These spin state effects have been alternatively attributed to doming of the porphyrin ring, with attendant loss of π conjugation,[4a,5a] or expansion of the porphinato core.[4b,5b] Both of these distortions would produce a weakening of the bonds at the methine bridges, and a decrease of the associated (or coupled) frequencies.

In the TPP spectra, two other polarized bands can be found, at ~1560 and ~390 cm^{-1}, whose frequency pattern parallels that of the ~1360-cm^{-1} band, as shown in Table II. The low value of the 1537-cm^{-1} frequency for the five-coordinate 2-methylimidazole Fe(II) derivatives is particularly notable. This band is well resolved from the corresponding band in the four- or six-coordinate Fe(II) complexes, and could be used as a specific monitor of five-coordination in equilibrium binding studies.

Reduction of Fe(TPP)Cl or Fe($T_{piv}PP$)Br in CH_2Cl_2 produced species whose Raman frequencies are very close to those of low-spin Fe(III) adducts, as was also observed for reduction of Fe(MP)Cl[5a] (MP = mesoporphyrin IX). This is as expected[5a] for four-coordinate intermediate-spin Fe(II) porphyrins, of which Fe(TPP) is a structurally well characterized example.[11a] The $d_{x^2-y^2}$ orbital is empty in these complexes, and the Fe-pyrrole bond is as short as in low-spin Fe(II) derivatives.

Fe-O_2 Stretch. The low-frequency spectrum of the "picket fence" dioxygen complex, Fe^{II}(TPP)(1-MeIm)O_2, shows a well-defined reproducible band at 568 cm^{-1} which disappears on passing argon through the solution (see Figure 2). As shown in Figure 3, the $^{18}O_2$ analogue exhibits a band at 545 cm^{-1} which disappears and is replaced by the 568-cm^{-1} band upon exposure to natural abundance O_2, confirming its assignment as $\nu(Fe-O_2)$. Its frequency corresponds closely to that of the $\nu(Fe-O_2)$ stretch of oxyhemoglobin, which occurs at 567 cm^{-1} and shifts to 540 cm^{-1} upon $^{18}O_2$ substitution.[7] This observation establishes the close similarity of the iron-oxygen bond in the complex and in oxyhemoglobin. Likewise the oxygen-oxygen stretch has been shown by infrared spectroscopy to be similar: 1159 cm^{-1} in the complex[12] and 1107 cm^{-1} [13] in oxyhemoglobin. It can be taken as established that oxyhemoglobin has the same bent Fe-O-O geometry as is found in the complex, and as was proposed by Pauling.[14]

Although the accuracy of the X-ray structure determination of the picket fence complex was reduced by disorder in the O_2 orientation, a distinctly short Fe-O bond, 1.75 Å, was suggested.[3] This is fully consistent with the high value of the Fe-O frequency, 568 cm^{-1}. This value may be compared with the Fe-O frequency, 500 cm^{-1}, observed for oxyhemerythrin,[15] in which the electron distribution is best described as
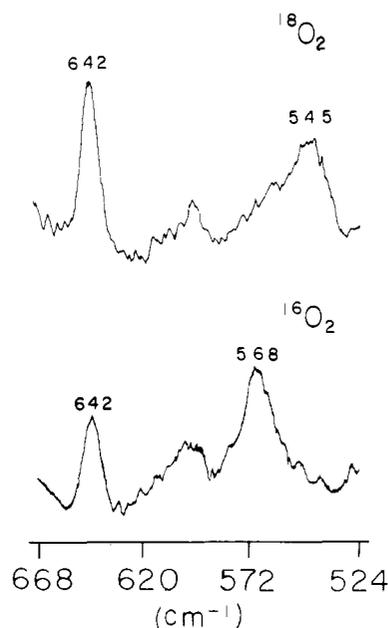
Figure 3. Resonance Raman spectrum of Fe($T_{piv}PP$)(1-MeIm)O_2 and $^{18}O_2$ analogue with 457.9-nm excitation. Concentration: 1 mg/mL in CH_2Cl_2.

$(Fe^{3+})_2(O_2^{2-})$ (although the geometry is unknown), or the Co-O frequencies, 500 and 493 cm^{-1},[16] in $[(NH_3)_5Co]_2O_2)^{5+}$ and $([(CN)_5Co]_2O_2)^{5-}$, in which Co^{3+} is bound to O_2^-. The strong Fe-O interaction is suggestive of multiple bonding, resulting from substantial π-back-donation from Fe(II) to O_2, with concomitant reduction in the O-O bond order to that of superoxide. This would also be consistent with the O-O stretching frequency,[12,13] and with the RR porphyrin frequencies of oxyhemoblobin. These are the same as those of low-spin Fe(III) hemes,[4a] suggesting that the extent of π-back-donation from Fe(II) to the porphyrin π^* orbitals is reduced upon O_2 binding to the same extent as upon oxidation to Fe(III).

References and Notes

(1) (a) Princeton University; (b) Stanford University.
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Electronic Structure of $M_4(CO)_{12}H_n$ and $M_4Cp_4H_n$ Complexes

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Abstract: The electronic structure of tetranuclear hydrido clusters $M_4(CO)_{12}H_n$ and $M_4Cp_4H_n$, $n = 3, 4, 6$, is analyzed with the aid of symmetry arguments and molecular orbital calculations. The orbitals of the clusters are derived by protonating $M_4(CO)_{12}$ and M_4Cp_4 tetrahedra. The important levels of these are the inward and surface-like higher occupied orbitals of $a_1 + e + t_2$ symmetry (plus a low-lying unfilled t_1 orbital occupied by three electrons in the electron-rich $Ni_4Cp_4H_3$ cluster). The electron distribution in the surface orbitals e and t_2 is studied as a function of staggered or eclipsed carbonyl orientation and along the edges or faces of the tetrahedron. The results of this study provide an understanding of the variable location of hydrogens in these clusters.

This paper is concerned with the electronic structure of tetranuclear hydrido clusters of the type $M_4(CO)_{12}H_n$ and $M_4Cp_4H_n$, Cp = cyclopentadienyl, M = a transition metal, and $n = 3, 4,$ or 6. The well-characterized molecules in this series share the basic feature of a near-tetrahedral disposition of the metal centers, but then diverge to exhibit staggered, **1**, or eclipsed, **2**, orientations of the carbonyl groups (relative to

1

2
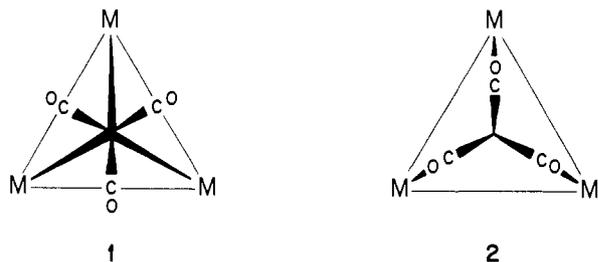
the metal–metal edges), and edge- or face-bridging hydrogens. They may also possess varying spin states and propensities to hydrogen mobility. This choice of geometrical and electronic structure is of interest to us.

Let us review what is known about these molecules, making reference only to well-established geometrical facts, and keeping in mind the problems associated with accurately locating hydride positions in X-ray crystallographic structures. $Re_4(CO)_{12}H_4$[2a] has four face-bridging hydrides and eclipsed carbonyl groups.[2b] $Re_4(CO)_{12}H_6{}^{2-}$ has staggered carbonyls, and the hydrides are presumably edge-bridging,[3] though this has not been definitely established. $Ru_4(CO)_{12}H_4$ has been synthesized[4] and a D_{2d} geometry with edge-bridging hydrides (**3**) established through X-ray diffraction.[5] In addition crystallographic studies on the derivatives $Ru_4(CO)_{11}$-$H_4P(OCH_3)_3$,[2b] $Ru_4(CO)_{10}H_4(PPh_3)_2$,[5] and $Ru_4(CO)_{10}$-$H_4(diphos)$[6] all show staggered carbonyls and four edge-bridging hydrides, though the disposition of the edges bearing hydrides differs: $Ru_4(CO)_{12}H_4$, $Ru_4(CO)_{11}H_4P(OCH_3)_3$, and $Ru_4(CO)_{10}H_4(PPh_3)_2$ have configuration **3**,[5] while

3

4
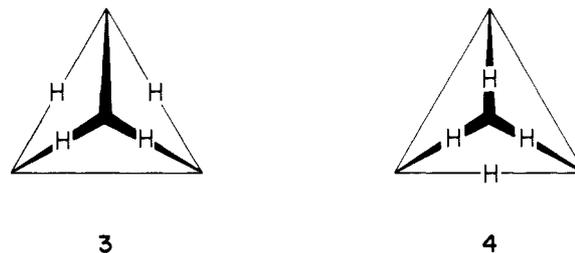
$Ru_4(CO)_{10}H_4(diphos)$ has configuration **4**. Hydride motions are complex and interesting in these Ru compounds.[4,6]

In the cyclopentadienyl complexes the question of eclipsing or staggering is a moot one, since the barrier of rotation of a fivefold rotor such as an η^5-cyclopentadienyl ring against the pseudo-threefold rotor presented to it by a metal vertex of the tetrahedron is expected to be small. $Co_4Cp_4H_4$ is known[7] and face-bridging hydrogens have been inferred from the crystal structure.[8] $Ni_4Cp_4H_3$ has also been synthesized[9] and has been studied by X-ray[10] and neutron[11] diffraction. Both methods concur in showing three face-bridging hydrogens. This compound is especially interesting because, in contrast to all molecules mentioned above, it is paramagnetic, with three unpaired electrons.[9]

The Orbitals of $M_4(CO)_{12}$

The natural construction of the electronic structure of the molecules is from the orbitals of tetrahedral $M_4(CO)_{12}$, **5**, or M_4Cp_4, **6**, interacting with three to six hydrogen atoms. In the real molecule the hydrogens may exhibit extremes of hydridic or protonic character, or some behavior in between—this will not affect our analysis which finds it convenient to begin with the formalism of an "electron-precise" or "saturated" cluster $Ir_4(CO)_{12}$ or Ni_4Cp_4 and to think of protonating that cluster or removing some electrons from it.

The electronic structure of these saturated clusters is well understood.[12-15] The $Ir(CO)_3$ and NiCp fragments are isolo-