high-spin structure. This frequency is much closer to the 6-coordinate than to the 4-coordinate ν_4 position, suggesting a substantial expansion of the porphyrin core on adding the first ligand, due to the $d_{x^2-y^2}$ orbital occupancy. The 7-cm^{-1} upshift relative to ν_4 of the high-spin 6-coordinate adduct can be attributed to partial relaxation of the core size due to the out-of-plane displacement of the Ni atom expected for a high-spin 5-coordinate adduct. A similar relaxation is seen for the 5-coordinate high-spin Fe^{II} complex (2-MeImH)FeTPP (2.45 Å, C_t–N; Fe 0.5 Å out of plane)[17] relative to the high-spin 6-coordinate adduct $(THF)_2$FeTPP (2.57 Å, C_t–N; Fe in plane).[18] Shelnutt et al.[9] have been able to determine RR bands for 5-coordinate NiPP from Ni-substituted myoglobin and hemoglobin, in which the proximal histidine side chain provides the single axial ligand. Again the frequencies are intermediate between those of 4- and 6-coordinate complexes.

Acknowledgment. This work was supported by Grant AC02-81ER10861 from the U.S. Department of Energy.

Registry No. Ni(OEP), 24803-99-4; Ni(PP), 15304-70-8; Ni(TPP), 14172-92-0; Ni[TPP(CN)$_4$], 104129-95-5; Ni[TPP(CN)$_4$](pip), 104129-96-6; Ni[TPP(CN)$_4$](pip)$_2$, 55835-72-8.

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Back-Bonding in Ruthenium Porphyrins As Monitored by Resonance Raman Spectroscopy

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Received March 17, 1986

Resonance Raman spectra are reported for Ru^{II} complexes of octaethylporphyrin (OEP) and tetraphenylporphine (TPP) with pyridine, methanol, and CO axial ligands, using both B- and Q-band excitation. For Ru^{II}OEP(CO)(MeOH) the porphyrin skeletal mode frequencies above 1370 cm^{-1} agree remarkably well with the values calculated on the basis of the porphyrin core size by using parameters derived earlier for iron protoporphyrin complexes. These frequencies shift both positively and negatively when the CO is replaced by pyridine due to π-back-donation from Ru to the porphyrin π^* orbitals. The shift pattern is the same as that observed for the bis(imidazole) adduct of iron(II) protoporphyrin, relative to the core size predictions, and the extent of the shifts is very similar in the two cases. Thus, π-back-bonding to the porphyrin appears to be quantitatively similar for Ru^{II} and Fe^{II}. π-Back-bonding shifts are also reported for Ru^{II}TPP(py)$_2$. For Ru^{II}OEP(CO)(py) the Ru–CO stretching, Ru–C–O bending, and C–O stretching modes are observed at 513, 578, and 1930 cm^{-1}. For Fe^{II} porphyrins, the M–CO and C–O frequencies are somewhat lower and higher, respectively, implying greater back-donation to the bound CO for Ru^{II} than for Fe^{II}.

Introduction

Ruthenium porphyrins have recently attracted interest because of their unusual electronic and chemical properties.[1–6] For Ru^{II}, back-bonding to π-acceptor ligands, including porphyrin itself, is a dominant feature of the chemistry. The situation is similar to that of Fe^{II} porphyrins, which are widespread in nature, and comparisons between the two are instructive. Back-bonding also plays a role in controlling the photoexcitation pathways for Ru^{II} porphyrins.[6] Thus, when both axial ligands are pyridine, the lowest excited state is short-lived (~12 ns) and is believed to be a d–π^* metal→porphyrin charge-transfer state, but when one of the ligands is CO, a longer lived (~70 μs) ${}^3(\pi-\pi^*)$ state is formed because back-bonding to the CO raises the energy of the d–π^* state.[6]

In this study we report resonance Raman spectra for CO and pyridine adducts of ruthenium(II) octaethylporphyrin (OEP) and tetraphenylporphine (TPP), with laser excitation in resonance with the B and Q absorption bands. The porphyrin skeletal modes are assigned with reference to the schemes that have been worked out for OEP[7] and TPP[8] complexes. Appreciable frequency shifts are associated with the presence or absence of bound CO, consistent with competition for π-back-bonding between the porphyrin and the CO π^* orbitals. The pattern is the same as has been observed for analogous Fe^{II} porphyrins,[9] and the extent of the shifts is quantitatively similar, suggesting comparable back-bonding to porphyrin from either Ru^{II} or Fe^{II}. The M–CO and C–O stretching frequencies, however, are higher and lower, respectively, for Ru^{II} than Fe^{II}, implying stronger back-bonding to CO from Ru^{II}.

RR spectra for RuOEP(py)$_2$ have been reported by Schick and Bocian,[5] who analyzed excitation profiles for both porphyrin and pyridine modes and compared them with the Fe and Os analogues. They assigned M→py charge-transfer transitions in the visible region and calculated excited-state distortions of the py ring, as Wright et al.[10] had done for the bis(pyridine) adduct of iron(II) *meso*-porphyrin. In the present work we have not been concerned with the pyridine enhancements.

Experimental Section

RuOEP(CO)(MeOH) and RuTPP(CO)(MeOH) were purchased from Porphyrin Products (Logan, UT) and used without further purification. The bis(pyridine) adducts were prepared by photolyzing the CO adducts in pyridine by using a tungsten lamp with a ultraviolet cutoff

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Table I. Resonance Raman Frequencies (cm^{-1}) for RuOEP(L)(L′) Complexes

	L,L′					
mode[a]	$(py)_2$[b]	CO,py[b]	CO,MeOH[c]	ν_{calcd}[d]	$\Delta(CO,MeOH-(py)_2)$[e]	$\Delta Fe^{II}(ImH)_2$[f]
ν_{10} (B_{1g})	1601	1606	1609	1607	−8	−17
ν_2 (A_{1g})	1584	1580	1579	1555	+5	+9
ν_{19} (A_{2g})	1563	1557	1559	1556	+4	+3
ν_{11} (B_{1g})	1530	1546	1548	1544	−18	−21
ν_3 (A_{1g})	1469	1473	1475	1478	−6	−5
ν_{28} (B_{2g})	1446	1446	1449	1443	−3	−3
ν_{29} (B_{2g})	1397	1400	1400			
ν_{20} (A_{2g})	1385	1385	1383			
ν_4 (A_{1g})	1357	1371	1371	1369	−14	−16
ν_{12} (B_{1g})	1359	1363	1363			
ν_{21} (B_{1g})	1311	1316	1314			
$\nu_5 + \nu_9$ (A_{1g})	1257	1257	1257			
ν_{13} (B_{1g})	1214	1214	1214			

[a] Mode numbering and assignments from ref 7b. [b] In pyridine. [c] In MeOH. [d] $\nu_{calcd} = K(A - d)$, where K (A) = 517.2 (5.16), 390.8 (6.03), 494.3 (5.20), 344.8 (6.53), 448.3 (5.35), 402.3 (5.64), and 133.3 (12.32) for ν_{10}, ν_2, ν_{19}, ν_{11}, ν_3, ν_{28}, and ν_4 (parameters obtained for Fe complexes of protoporphyrins[9,18]) and d = 2.052 Å, the C_t–N distance for RuOEP(CO)(py).[19] [e] $\nu_{RuOEP(py)_2} - \nu_{RuOEP(CO)(MeOH)}$. [f] Frequency for Fe^{II}(protoporphyrin)(imidazole)$_2$ minus ν_{calcd} for its C_t–N, 2.004 Å.[9]

filter.[11] The pyridine was then evaporated, and the bis(pyridine) adducts were dissolved in methylene chloride and chromatographed on alumina A-540 (Fisher) to remove minor impurities. As noted by Schick and Bocian,[5] the bis-(pyridine) adduct is unstable in methylene chloride due to photooxidation. We ran their RR spectra in pyridine and found no decompostion.

Raman spectra were obtained with a Spec 1401 double monochromator, equipped with a cooled photomultiplier and photon-counting electronics. The data were collected digitally with a MINC (DEC) computer. Excitation lines at 406.7, 413.1, 514.5, 520.8, and 530.9 nm were provided by Kr^+ and Ar^+ lasers. Relatively low laser power levels were used in order to avoid photodegradation of the samples.

Results

Figure 1 compares RR spectra with 406.7-nm excitation, in resonance with the B bands for RuOEP$(py)_2$, RuOEP(CO)(py), and RuOEP(CO)(MeOH) (λ_{max} = 395, 396, and 393 nm, respectively), the latter in MeOH and in CH_2Cl_2 solution. The bands are readily assigned with reference to the modes of NiOEP[7] (see Table I). With β-band excitation, the RR spectra are dominated by the totally symmetric A_{1g} modes ν_2, ν_3, and ν_4 at 1579, 1475, and 1371 cm^{-1} (for the CO adducts), but appreciable intensities are also seen for B_{1g} modes (ν_{10}, ν_{11}, and ν_{13} at 1609, 1548, and 1214 cm^{-1} for the CO adducts) presumably due to Jahn–Teller effects in the degenerate excited states.[12] The spectra are the same for the complexes containing CO, whether the opposite ligand is pyridine or methanol. In CH_2Cl_2, RuOEP(CO)(MeOH) is known[13] to be largely dissociated into RuOEP(CO) and MeOH. Yet there is no discernable difference in the spectra. It must be concluded that, insofar as the porphyrin mode frequencies and intensities are concerned, the CO ligand dominates the situation, and the identity of the trans axial ligand or its absence makes no difference to the spectra. Large frequency shifts are seen, however, for RuOEP$(py)_2$.

The same situation is encountered with Q-band excitation, as shown in Figure 2. With 530.9-nm excitation the inverse polarized A_{2g} modes (ν_{19}, ν_{20}, and ν_{21} at 1557, 1385, and 1316 cm^{-1} in the CO adducts) are dominant, while B_{1g} and B_{2g} modes are seen more weakly, and A_{1g} modes are absent. Slight differences, 2–3 cm^{-1}, can be seen for some of these modes between the CO adducts with pyridine and methanol as trans ligands. Again, much larger changes are seen for RuOEP$(py)_2$. The frequencies and assignments are listed in Table I. We note that the frequencies reported by Schick and Bocian[5] for RuOEP$(py)_2$ are appreciably higher than ours. In part this may be due to medium effects, their spectra being obtained with sodium sulfate pellets, but we suspect that their sample may have been partially oxidized: conversion to Ru^{III} would have the effect of reducing π-back-bonding to porphyrin and altering the skeletal mode frequencies, just as CO binding does. For example, the ν_4 value reported by Schick and Bocian, 1372 cm^{-1}, coincides with our value for Ru(OEP)(CO)(py) while we observe ν_4 at a much lower frequency, 1357 cm^{-1}, for RuOEP$(py)_2$.

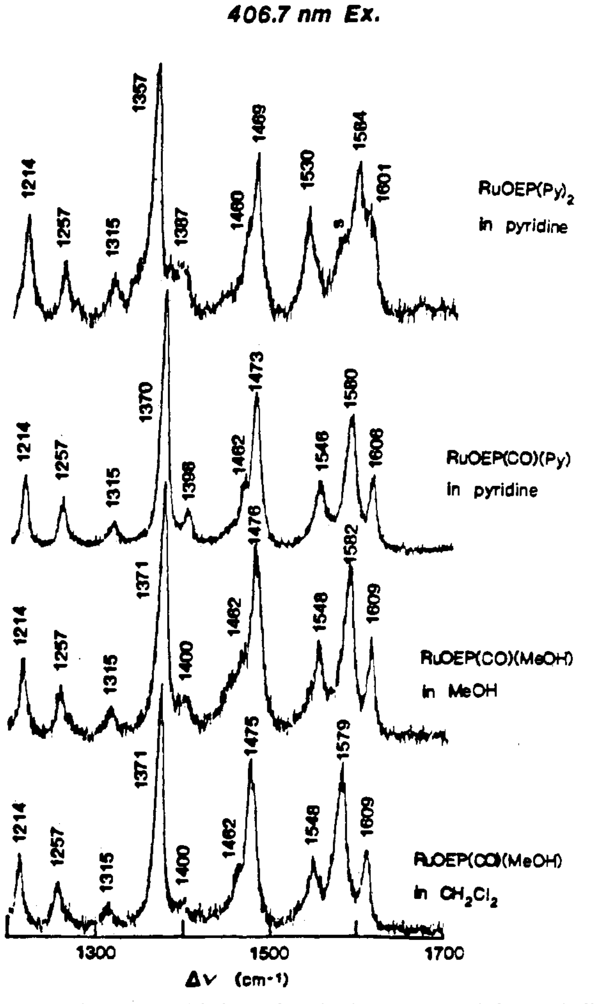

Figure 1. RR spectra with B-band excitation (406.7 nm) for the indicated OEP species (~1 mM). Conditions: laser power, 10 mW; slit width, 5 cm^{-1}; scan rate, 0.5 cm^{-1}/s.

Figure 3 compares low-frequency spectra, obtained with 406.7-nm excitation, for the bis(pyridine) and CO–pyridine adducts. The 472-cm^{-1} band is a porphyrin mode, probably arising

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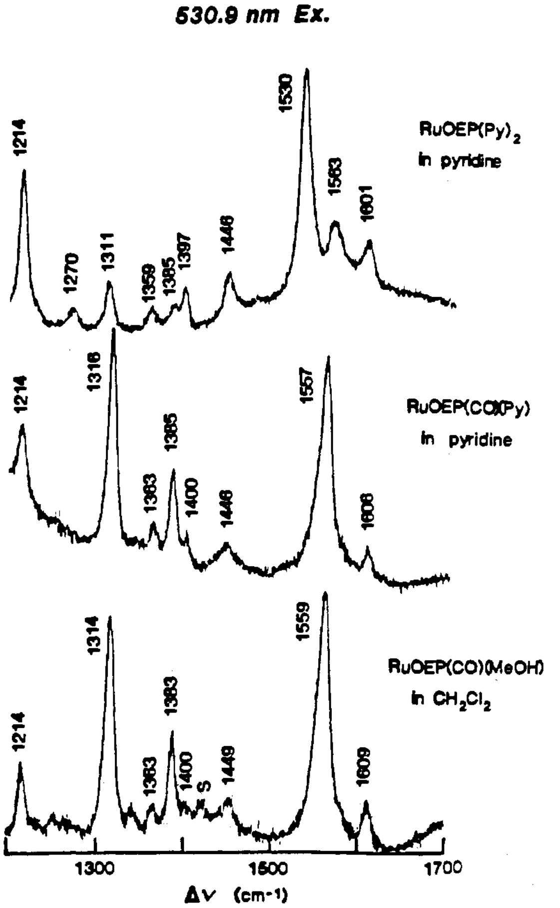

Figure 2. RR spectra with Q-band excitation (530.9 nm) for the indicated OEP species (~3 mM). Conditions: laser power, 30 mW; slit width, 5 cm^{-1}; scan rate, 0.5 cm^{-1}/s.

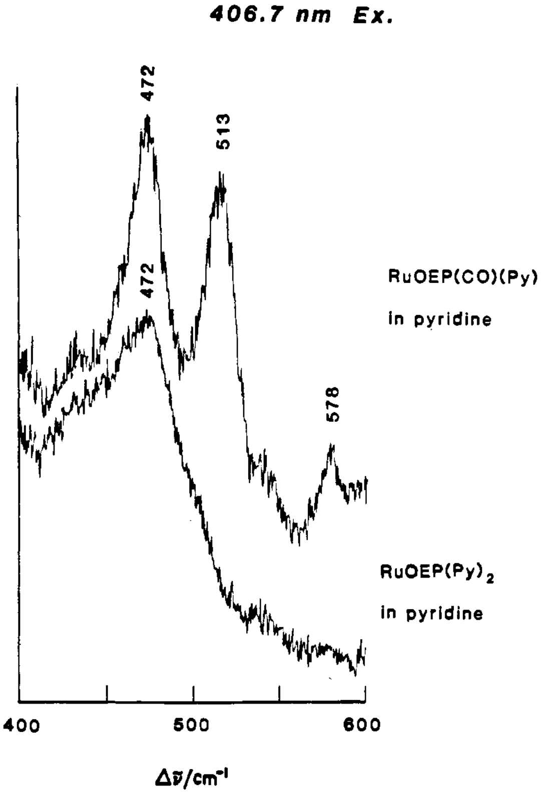

Figure 3. Low-frequency, B-band-excited RR spectra for RuOEP(CO)(py) and RuOEP(py)$_2$, showing bands assigned to ν_{Ru-CO} (513 cm^{-1}) and δ_{Ru-C-O} (578 cm^{-1}) for the former. Conditions: laser power, 10 mW, slit width, 5 cm^{-1}; scan rate, 0.5 cm^{-1}/s.

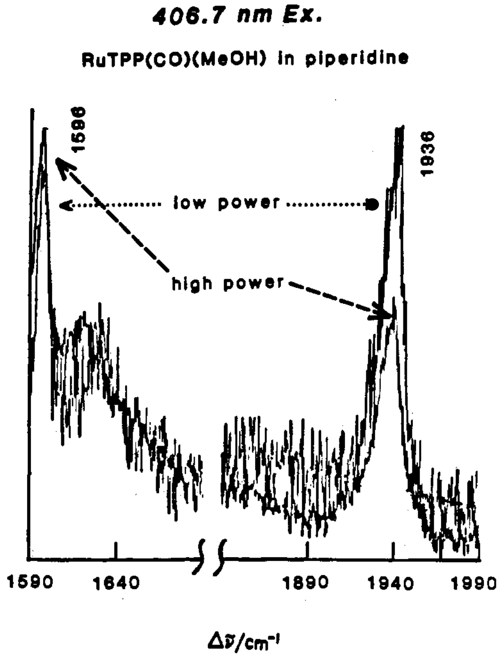

Figure 4. High-frequency, B-band-excited RR spectra for RuTPP(CO)(MeOH) in piperidine, showing loss in ν_{CO} (1936 cm^{-1}) mode intensity at high laser power as the CO is photolyzed and replaced with piperidine. Conditions are as in Figure 3.

Table II. RR Frequencies (cm^{-1}) for RuTPP(L)(L′) Complexes

	L,L′		
mode[a]	(py)$_2$[b]	CO,py[b]	Δ(CO,py–(py)$_2$)[c]
$\nu_3 + \nu_{35}$ (B$_{1g}$)[d]	1647	1649	
A (phenyl)	1596	1596	
ν_{11} (B$_{1g}$)	*e*	*e*	
ν_2 (A$_{1g}$)	1542	1542	
ν_{20} (A$_{2g}$)	1516	1509	+7
$\nu_5 + \nu_8$ (A$_{1g}$)[d]	1490		
ν_{12} (B$_{1g}$)	1467	1487	−20
$\nu_{14} + \nu_{17}$ (A$_{1g}$)[d]		1460	
ν_3 (A$_{1g}$)	1434	1438	−4
ν_{28} (B$_{2g}$)	1362	1363	−1
ν_4 (A$_{1g}$)	1351	1356	−5
ν_{21} (A$_{2g}$)	1323	1326	−3
ν_{13} (B$_{1g}$)	1263	1269	−6
ν_{22} (A$_{2g}$)		1241	
C (C$_m$ – Ph)	1226	1231	−5

[a] Mode labels and assignments from ref 8. [b] In pyridine. [c] $\nu_{RuTPP(py)_2} - \nu_{RuTPP(CO)(py)}$. [d] Tentative assignments of weak bands to combination modes at positions near those expected for (FeTPP)$_2$O.[8] [e] Expected near 1560 cm^{-1}; obscured by solvent.

from pyrrole out-of-plane bending.[14] Two additional bands are seen in the CO adduct, at 513 and 578 cm^{-1}. These are assignable to Ru–CO stretching and Ru–C–O bending, by analogy with similar bands observed for FeCO porphyrins. For example, the CO adduct of myoglobin shows Fe–CO stretching and Fe–C–O bending modes at 507 and 578 cm^{-1},[15] while the Fe–CO stretch of the imidazole adduct of FeCO protoporphyrin in CH$_2$Cl$_2$ is at 495 cm^{-1}.[16] Figure 4 shows high-frequency spectra with 406.7-nm excitation for RuTPP(CO)(MeOH) and piperidine solvent. The band at 1936 cm^{-1} is readily assigned to C–O stretching, while the 1598-cm^{-1} band is a phenyl mode of TPP. Both bands are relatively weak; the C–O stretch can be also be seen weakly in RR spectra of CO–heme proteins obtained with B-band excitation.[15] At high laser power levels photolysis of the CO leads to a diminution of the 1936-cm^{-1} band in RuTPP-

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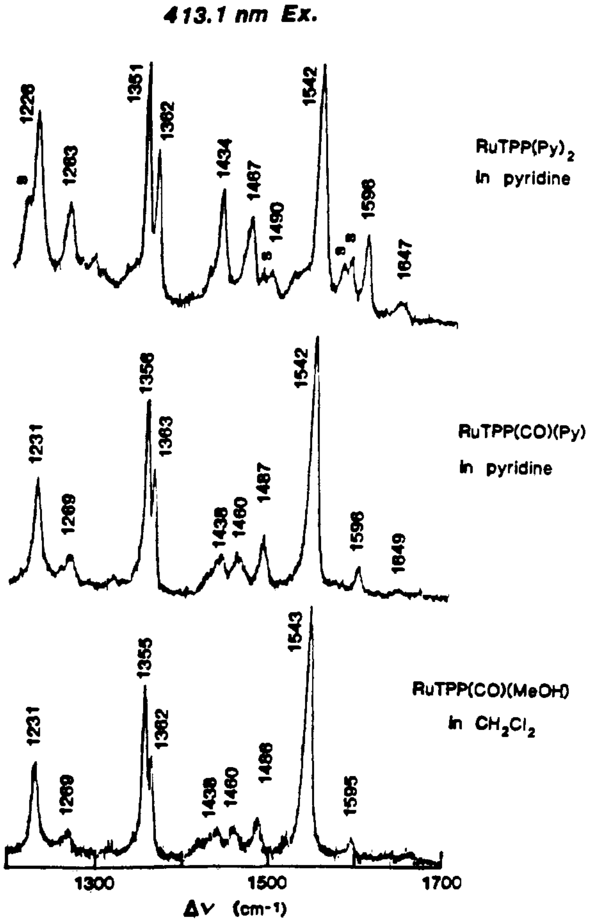

Figure 5. RR spectra with B-band excitation (413.1 nm) for the indicated TPP species. Conditions are as in Figure 1.

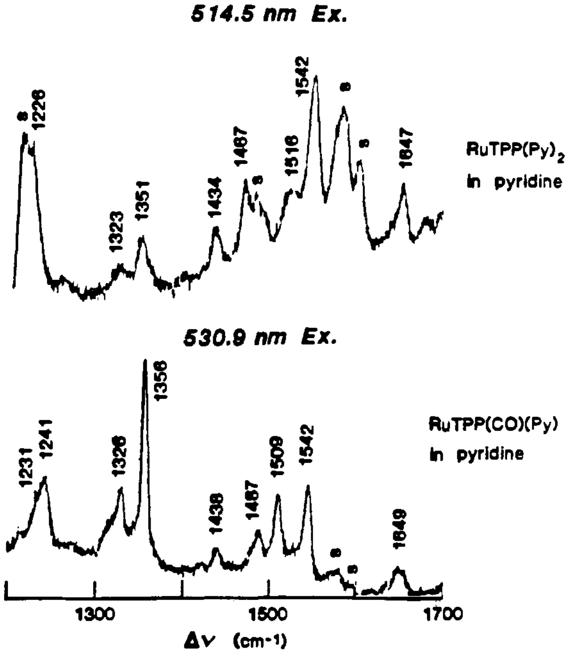

Figure 6. RR spectra with Q-band excitation (514.5 or 530.9 nm) for the indicated TPP species. Conditions are as in Figure 2.

(CO)(MeOH). Likewise, when RuOEP(CO)(py), for which ν_{CO} = 1930 cm^{-1}, is irradiated at high power levels in pyridine, the spectrum gradually converts to that of RuOEP(py)$_2$.

Figures 5 and 6 show B- and Q-band RR spectra for RuTPP bis(pyridine) and CO–pyridine adducts. The bands are listed and assigned in Table II. As with the OEP adducts, significant differences are observed when CO is replaced with pyridine.

Discussion

Systematic studies of iron porphyrins have shown the frequencies of the porphyrin skeletal modes above 1450 cm^{-1} to be sensitive principally to two factors:[9] (1) the core size of the porphyrin ring, as determined by the properties of the central metal ion and the axial ligands, and (2) the electronic effects of π-back-donation from the metal to the ring. Recently the frequency of the C–N breathing mode, ν_4, which is sensitive to electronic factors associated with the metal oxidation state, has also been shown to be responsive to the core size.[17,18] In Table I we list the frequencies calculated from the empirical core size parameters[9,18] for a porphyrin with a 2.052-Å, center-to-nitrogen (C$_t$–N) distance, the value determined crystallographically for RuOEP(CO)(py).[19] The numbers are seen to correspond well to the experimental values for RuOEP(CO)(py). (We note that C$_t$–N is nearly the same, 2.049 Å, for RuTPP(CO)(EtOH);[20] all the frequencies are predicted to be 1–2 cm^{-1} higher, consistent with the slight upshifts observed for RuOEP(CO)(MeOH).) The agreement is the more remarkable in that the parameters were derived for iron protoporphyrin complexes.[9] The one discrepancy beyond 4–5 cm^{-1} is observed for ν_2 (1556 cm^{-1} calculated, 1580 cm^{-1} observed). This is known to be associated with a specific depression of ν_2 in protoporphyrin relative to that of octaethylporphyrin due to vibrational coupling between ν_2 and vinyl C=C stretching.[9] It must be concluded that RuOEP(CO)(py) behaves very much like an iron porphyrin of the same size. While the core size of RuOEP(py)$_2$ is nearly unchanged (2.047 Å),[11] the RR frequencies differ substantially from those of RuOEP(CO)(py).

In the case of the bis(imidazole) adduct of iron(II) protoporphyrin, strong deviations from the core size correlations were noted.[9] These shifts were attributed to Fe→prophyrin back-bonding and could plausibly be related to the nodal properties of the porphyrin e$_g$* orbital. In particular the strong downshifts found for ν_{10} and ν_{11} were related to the fact that the B$_{1g}$ motions are in phase for equivalent bonds on opposite pyrroles and out of phase for these bonds on adjacent pyrroles; this phasing is the same as that of the e$_g$* nodal pattern.[9] The shifts relative to the core size predictions are listed for Fe^{II}PP(ImH)$_2$ in Table I and compared with the frequency difference between the bis(pyridine) and CO–pyridine adducts of RuOEP. The patterns are seen to be the same, upshifts being observed for ν_2 and ν_{19} and downshifts for the remaining modes. Particularly large downshifts are seen for ν_{11} and ν_4, although the ν_{10} downshift is somewhat less for Ru^{II} than for Fe^{II}. Aside from this difference, the shifts are nearly equal in the two cases. Thus we conclude that the back-bonding from the central metal to the porphyrin ring occurs to nearly the same extent for Ru^{II} and Fe^{II}. Bound CO competes effectively for the Ru dπ electrons and relieves the back-bonding effects on the OEP frequencies. A similar effect was observed in early studies of Fe porphyrins and provided the original evidence for a strong back-bonding influence on the porphyrin frequencies.[21,22]

Similar frequency shifts are expected for TPP adducts but have not previously been documented. Although the normal modes fall in the same symmetry classes, their compositions differ appreciably for TPP and OEP because of the altered substituent pattern and the associated changes in vibrational coupling.[8] Nevertheless, Table II shows that a large downshift is seen for the bis(pyridine) adduct ν_{12} B$_{1g}$ mode similar to the ν_{11} downshift seen for OEP, and likewise a modest upshift for the ν_{20} A$_{2g}$ mode similar to that of the ν_{19} mode of OEP is seen. (We note that the numbering system for TPP[8] is shifted relative to that of OEP[7] because of the extra C–H stretches associated with the eight pyrrole H atoms.)

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The remaining skeletal modes show small downshifts. The mode at 1596 cm^{-1}, localized on the phenyl ring, does not shift, consistent with the expected lack of significant phenyl conjugation, the peripheral phenyl groups being twisted out of the porphyrin plane; steric hindrance with the pyrrole C$_b$H atoms provide a substantial barrier to rotation.[23] This observation strengthens the inference[24] that the resonance enhancement of the phenyl modes in TPP is due not to ground-state conjugation but rather to a displacement of the phenyl rings toward coplanarity in the excited state.

The substantial back-donation implied by the porphyrin frequency shifts in the bis(pyridine) adducts are consistent with the molecular orbital calculations of Gouterman and co-workers.[2,3] Replacement of pyridine by CO abolishes the back-bonding effects on the porphyrin frequencies; the frequencies displayed by the CO adducts of RuOEP are just those expected on the basis of the porphyrin core size. Thus, CO competes very effectively withporphyrin for the Ru dπ electrons. Indeed, the bound CO so dominates the electronic structure that the same porphyrin frequencies are seen whether the trans axial ligand is pyridine or MeOH or when there is no trans ligand at all. Direct evidence for the strong back-donation to CO is seen in the C–O stretching frequency, 1930 cm^{-1}, which is 30 cm^{-1} lower than that shown by Fe^{II}PP(CO)(ImH) in the same solvent, CH$_2$Cl$_2$.[15] The Ru–CO frequency 513 cm^{-1}, is 18 cm^{-1} higher than the Fe–CO stretch of this complex.[15] For the same force constants, a somewhat lower M–CO frequency would be expected for the Ru adduct, due to the greater metal atom mass. Thus, the frequency upshift actually observed is an indication of significantly stronger bonding, consistent with greater back-donation to CO from Ru^{II} than from Fe^{II}.

The observation of the Ru–C–O bending mode at 578 cm^{-1} is of interest. This band has been observed in several heme proteins,[15,16] but it is not seen in protein-free heme CO complexes except in the case of a strapped porphyrin,[25] and the observation of this band has therefore been associated with tilting of the Fe–C–O linkage.[15] There is no reason to expect the Ru–C–O linkage to be tilted in RuOEP(CO)(py), and in this case the observation of the bending mode in the RR spectrum must be a purely electronic effect, perhaps associated with the increased back-donation from Ru.

Acknowledgment. We thank Professor Dewey Holten for samples of Ru(OEP)(py)$_2$ and Ru(TPP(py)$_2$ and for helpful discussions. Special thanks are extended to Kwang-Hyun Ahn who provided RuTPP(CO)(CH$_3$CN) and RuTPP(py)$_2$. This work was supported by Grant AC02-81ER10861 from the U.S. Department of Energy.

Registry No. Ru(TPP)(py)$_2$, 34690-41-0; Ru(TPP)(CO)(py), 41751-82-0; Ru(TPP)(CO)(MeOH), 89555-37-3; Ru(OEP)(py)$_2$, 54762-60-6; Ru(OEP)(CO)(py), 38478-17-0; Ru(OEP)(CO)(MeOH), 89530-39-2.

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Electronic Structure of Transition-Metal Tetracoordinated Complexes. 1. Theoretical ab Initio and UV–Photoelectron Spectroscopy Study of Palladium(II) and Platinum(II) Square-Planar Acetylacetonate Complexes

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Received August 8, 1985

The electronic structures of Pd(acac)$_2$ and Pt(acac)$_2$ have been studied by using the pseudopotential valence-only ab initio method (including corrections for the major relativistic effects in the case of the heavier metal complex) and combined He I and He II photoelectron spectroscopy. A remarkable metal–ligand covalency involving orbitals of σ and π symmetry emerges from the analysis of the theoretical results. In particular, interactions with orbitals of σ symmetry involve empty s and d$_{xy}$ metal orbitals and results in important ligand-to-metal charge transfer. These effects are both of a major importance in the case of the Pt complex. Detailed assignments of the UV photoelectron spectra are proposed on the basis of results of a simple perturbative treatment to correct the Koopmans eigenvalues for the reorganization effects in the ion states. Ionization energy values associated to production of selected ion states have been also evaluated by a ΔSCF treatment. The relative intensity changes of low-ionization-energy photoelectron bands observed on passing from the He I to the He II excited spectra have proven to be crucial guidance for the final assignments.

Introduction

Considerable attention has been focused on the electronic structures of tetracoordinated square-planar complexes of d^8 metal(II) ions. Efforts have been directed to rationalize their high reactivities and kinetical labilities[2] as well as to understand their anticancer[3] and unusual solid-state electric properties.[4] Nevertheless, the large number of investigations have left still uncertain the energy sequence of the upper filled molecular orbitals (MO's).[5]

In this context, UV–vis optical spectroscopy was first used within a crystal field methodological approach.[5c,d,6] However, it quickly became evident that this approach was only capable of providing the sequence of electronic excitations rather than of MO energy levels.[7] Later on, gas-phase UV photoelectron spectroscopy (PES) data were used, within the Koopmans' approximation,[8] to map the energy of the outermost occupied MO's

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