Porphyrins. 38.[1] Redox Potentials, Charge Transfer Transitions, and Emission of Copper, Silver, and Gold Complexes

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Abstract: While Cu^{II} porphyrins are known to luminesce, Ag^{II} complexes do not. It is shown here that silver(III) octaethylporphyrin has no emission while gold(III) tetraphenylporphyrin has a moderately intense phosphorescence with a nonexponential decay fit with two decay times of 63 and 184 μs. In contrast to Cu^{II} and Au^{III} porphyrins, the Ag complexes have a metal redox potential, $II \rightleftharpoons III$, between that of ring oxidation and ring reduction suggesting that luminescence is quenched by low-energy charge transfer transitions $Ag^{II} \rightarrow$ ring or ring $\rightarrow Ag^{III}$. Near-infrared (1100–700 nm) absorption spectra confirm the presence of weak absorption bands in Ag^{II} and Ag^{III} complexes that are not observed in complexes of Cu^{II} and Au^{III}. The near-IR absorption of $Cu^{II}(TPP)$ and the quenching of its unusually broad emission by pyridine suggest that a charge transfer state is close to the emitting level. Iterative extended Hückel calculations explain these facts by the energy of orbital $b_{1g}(d_{x^2-y^2})$, which rises along the series Cu < Ag < Au.

Introduction

A recent electronic taxonomy of metalloporphyrins provides a framework for understanding the vast array of optical absorption and emission data and highlights the areas where the biggest questions remain.[3] Metalloporphyrins with partly filled d shells (hemes being in this group) exhibit a variety of spectra and are not completely understood. In this paper we present further investigation on the electronic structure of group 1B (Cu, Ag, Au) metalloporphyrins.

In our previous work we have attributed lack of emission in metalloporphyrins to low-energy states not of (π,π^*) character: charge transfer (CT),[3,4] (d,d),[5] or (f,f)[6] transitions. We have further hypothesized that if charge transfer states are the cause, their presence at low energy should correlate with metal redox potentials.[4,7]

In this paper we explore this problem for Cu, Ag, and Au complexes of octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP). The copper porphyrins are long known as having metal valence Cu^{II}[8,9] and strong emission from the tripdoublet state.[10-12] The silver porphyrins show a redox reaction $Ag^{II} \rightleftharpoons Ag^{III}$[13] and have no luminescence.[14,15] (A bimetallic Ag^{I} species has also been reported.[8]) Gold porphyrin has been reported to be Au^{III}.[16a] At the time we began this study there were no reports of emission or redox properties of Au^{III} porphyrins; however, a detailed study of their redox properties has recently been published.[16b]

The aim of this paper is to show that in Cu, Ag, and Au porphyrins lack of emission correlates with low-energy charge transfer transitions. We do this through an examination of (1) visible–near-UV absorption spectra, (2) emission spectra, (3) redox potentials, and (4) near-IR absorption data. We shall survey older data and report new data. We shall also report on iterative extended Hückel (IEH) calculations, and show the extent to which they rationalize the data.

Experimental and Calculational Methods

Preparations. $Ag^{II}(OEP)$,[17] $[Ag^{III}(OEP)][ClO_4]$,[18] and $[Au^{III}(TPP)][AuCl_4]$[16] were prepared by literature methods. $[Ag^{III}(OEP)][PF_6]$ was prepared by controlled-potential electrolysis of $Ag^{II}(OEP)$ at 0.65 V vs. Ag/AgCl. Simultaneous coulometric measurement showed $n = 1$, indicative of a one-electron oxidation. $Ag^{II}(TPP)$ was prepared by refluxing 100 mg of TPP in 100 mL of acetic acid. Solid $AgNO_3$ (0.277 g, tenfold excess) was added along with 100 mg of sodium acetate. The suspension was allowed to reflux for 45 min, cooled to room temperature, filtered, and washed with copious amounts of water. The purple crystals were recrystallized from CH_2Cl_2–CH_3OH. The copper complexes had been prepared by the usual methods.[17]

Electrochemistry. All electrochemical measurements were recorded in dried, redistilled CH_2Cl_2, which was stored over 4 Å sieves. The supporting electrolytes were tetra-*n*-butylammonium hexafluorophosphate or tetra-*n*-butylammonium perchlorate, which were recrystallized and dried in vacuo prior to use. The reference electrode used was the Ag/AgCl electrode, and values obtained have been converted to potentials vs. SCE for comparison with previously published values. Bulk electrolyses were performed on a PAR Model 173 using a Model 176 electrometer probe. The cyclic voltammograms were recorded on standard operational amplifier circuitry, as described previously.[19]

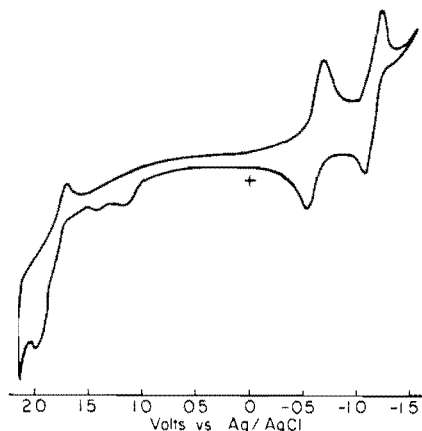It was found that cyclic voltammetric measurements were repro-

Figure 1. Cyclic voltammogram for [Au^{III}(TPP)]$^+$ in 0.1 M tetra-*n*-butylammonium hexafluorophosphate in CH$_2$Cl$_2$ after preelectrolysis at 0.5 V.

Figure 2. Absorption spectrum of [Au^{III}(TPP)][AuCl$_4$] at room temperature in CH$_2$Cl$_2$.

ducible during only the first cycle of the [Au^{III}(TPP)][AuCl$_4$], and close subsequent inspection of the Pt bead working electrode showed the presence of gold film on the bead. This problem was overcome by preelectrolysis of the solution at 0.5 V to remove the AuCl$_4^-$, after which cleaner and more easily interpreted cyclics were recorded, as shown in Figure 1. A similar approach was taken by Jamin and Iwamoto.[16b]

Optical Spectra. All absorption spectra (near-UV, visible, near-IR) were taken on a Cary 14 spectrophotometer. Spectra were taken on freshly prepared solutions; the solvent for all was spectroquality dichloromethane.

Emission and lifetime measurements have been carried out as described previously.[4] Excitation spectra showed that the reported emission came from the main absorbing species. The compounds reported as nonemitting showed some weak or spurious peaks which did not belong to the main absorbing species. The solvent for emission studies of Ag and Au complexes was a mixture of ethanol and glycerol (11:1), which forms a cracked glass at low temperature; the compounds were not soluble in common glass forming solvents.

All Ag and Au complexes discussed here and Cu(TPP) were examined for emission in liquid nitrogen (77 K) in the spectral range 600–850 nm with an RCA 8852 photomultiplier tube. [AuTPP]-[AuCl$_4$] was also studied at room temperature in ethanol–glycerol (11:1), in CH$_2$Cl$_2$, and in acetone solutions, which were degassed by bubbling argon as described previously.[4]

Iterative Extended Hückel Method. The iterative extended Hückel method and the program used have been previously reported along with parameters for H, C, N, and Cu.[24] The atomic orbital ionization potentials for Ag and Au were determined from the atomic energy levels reported by Moore[25] in the manner described by Zerner. To determine the orbital exponents, we followed the method described recently.[4]

The geometry of the planar porphyrin ring was the same as that used previously[24] except for displacement of the N atoms in accord with metal–nitrogen bond distances (Cu–N, 2.00 Å; Ag–N, 2.10; Au–N, 2.10). These distances have been obtained from crystal structure studies of Cu and Ag porphyrins[26] and from covalent radii consideration for [Au^{III}(TPP)]$^+$.

The orientation of the porphyrin molecules with respect to coordinate axes was such that the center of the coordinate system coincided with the center of the porphyrin plane and the nitrogens were on the *x,y* axes. All atoms were in the *x–y* plane. The calculations reported here were done on the unsubstituted porphine (P) ring. Calculations on Cu(TPP) gave a slightly lower energy for the (π,π^*) transitions compared to Cu(P), but the d orbital was little affected.

Experimental Results

Since there has been considerable work on the visible–UV absorption, emission, and redox potentials of Cu, Ag, and Au porphyrins, we have systematically listed references to earlier data in Table I. A review of porphyrin electronic spectra has been given recently.[3,4] Various absorption and emission types
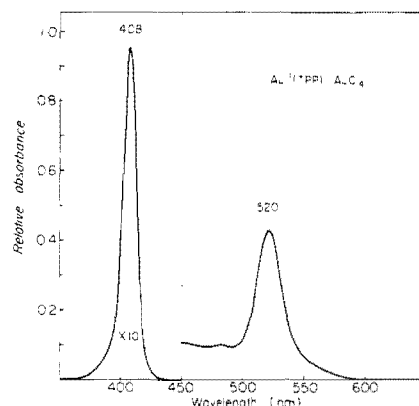
were defined there. We shall use that terminology in our discussion here, indicating these special terms by italics.

Visible–Near-UV Absorption. The Cu, Ag, and Au metalloporphyrins show the expected visible *Q* and near-UV *B* bands attributed to ring (π,π^*) transitions. All the spectra are blue shifted compared to a closed d-shell metalloporphyrin *normal* spectrum and thus can be classified as *hypso*.[3] This blue shift is very small for the Cu^{II} and Ag^{II} complexes and is somewhat larger for (TPP) than for (OEP). The blue shift is greater for the Ag^{III} and Au^{III} metalloporphyrins. In room temperature absorption in CH$_2$Cl$_2$, [Au^{III}(TPP)][AuCl$_4$] shows clearly only two bands: the Soret band at 408 nm and the Q(1,0) (or β) band at 520 nm (Figure 2). In the phosphorescence excitation spectrum in ethanol–glycerol (11:1) at 77 K the spectrum shows greater resolution and the following bands appear in addition to the Soret: a weak shoulder (450–460 nm); a weak broad band (485–490 nm); the strong Q(1,0) (526 nm); and a weak Q(0,0) (or α) band (560 nm). The band at 450–460 nm we attribute to (π,d) charge transfer; the band at 485–490 nm may be either (π,d) charge transfer or Q(2,0). Because there are two top filled orbitals, a$_{1u}(\pi)$ and a$_{2u}(\pi)$, two (π,d) CT bands are possible.

Emission Spectra. The emission spectra of Cu^{II} complexes have been known for some time (Table I) and are attributed to emission from the "tripdoublet" and "tripquartet" (^{2}T$_1$, ^{4}T$_1$) that arise when the odd electron of the Cu^{II} couples to the spin of the ring triplet, ^{3}T$_1$.[10-12] In contrast, earlier studies on silver(II) mesoporphyrin[14] (Meso) and silver(II) etioporphyrin[15] found no emission. We examined the three silver complexes listed in Table I for emission, but none was found. We estimate that an upper limit for the phosphorescence quantum yield between 600 and 850 nm is $\Phi_p < 3 \times 10^{-4}$.

Emission from [Au^{III}(TPP)]$^+$ has not been previously reported. We could find no fluorescence, but a phosphorescence (Figure 3) is easily observed. Comparison to zinc etioporphyrin emission allows us to estimate the phosphorescence quantum yield as $\phi_p \sim 6 \times 10^{-3}$. Its decay at 77 K in a mixture of ethanol and glycerol (11:1) is nonexponential. It can be fit to a decay $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ with $A_1/A_2 = 1.1$ and $(\tau_1,\tau_2) = (63 \pm 14, 184 \pm 6)$ μs. The double lifetime may be due to slow relaxation among triplet sublevels. However, the presence of two closely related species is another possibility, since on standing at room temperature for several hours the emission spectrum changed slightly. Degassed room temperature solutions showed no emission. We take this as indicating possible quenching due to thermal population of a charge transfer state. A similar case was recently observed for the complex Os(OEP)NO(OCH$_3$).[4] (The absence of emission in a degassed solution may, of course, arise from collisional quenching; our qualitative observation is therefore suggestive, not conclusive.)

Table I. Data on Electronic Spectra and Redox Potentials[a]

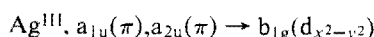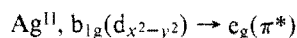| compd	vis–UV	emission	redox potentials (vs. SCE), V			
			$E_{1/2}^+(1)^d$	$E_{1/2}(II \rightleftharpoons III)$	$E_{1/2}^-(1)^d$	ref
Cu^{II}(TPP)	see ref 8[b]	see ref 10	[0.99]		[−1.20]	21, 22
Cu^{II}(OEP)	see ref 9, 10[b]	see ref 10	[0.79]		[−1.46]	23
Ag^{II}(TPP)	see ref 8[b]	none[b]	1.64	0.55	~−1.1	b
Ag^{II}(OEP)	see ref 13, 20[b]	none[b] (ref 14, 15)[c]	1.51	0.45	−1.20	b
			[1.10][e]	[0.44]	[−1.29]	23
[Ag^{III}(OEP)][X]	see ref 13[b]	none[b]	1.48	0.44	−1.17	b
[Au^{III}(TPP)][AuCl$_4$]	Figure 2,[b] ref 16	Figure 3[b]	1.68		−0.59	b
			[1.68]		[−0.52]	16b

[a] Data from references in brackets. [b] Data determined or repeated in this work. [c] References 14 and 15 report no emission from silver(II) mesoporphyrin and silver(II) etioporphyrin, respectively. [d] $E_{1/2}^+(1)$ is first ring oxidation potential; $E_{1/2}^-(1)$ is first ring reduction potential; $E_{1/2}(II \rightleftharpoons III)$ is for metal oxidation. Data in brackets from references indicated. [e] The solvent here is *n*-butylnitrile; our data is taken in CH$_2$Cl$_2$. This may explain the different $E_{1/2}^+(1)$.

Two earlier features of the emission of Cu^{II} porphyrins also suggested the existence of a charge transfer state that affects triplet emission. (1) For Cu^{II}(Meso) it was found that in Lucite samples phosphorescence emission is strongly quenched above 77 K,[12] although this is not found for other porphyrins, e.g., Zn, Pd, or Pt.[27] (2) For Cu^{II}(TPP) the emission is anomalously broad, and at 77 K the emission decay is nonexponential with three decay times.[10,12]

Because the Cu^{II}(TPP) emission is so anomalously broad, it seemed likely that the emission was being perturbed by a close-lying CT transition. We therefore studied the Cu^{II}(TPP) emission in pyridine, a σ donor which presumably should lower the energy of the (d,π^*) charge transfer state by putting electron density on the metal. We observed that in pyridine the luminescence is quenched. Since pyridine forms a snow, an effect that often reduces the observed emitted light, we repeated these studies in a 1:1 mixture of pyridine–tetrahydrofuran, which forms a cracked semiglass, and compared the emission with that of Cu^{II}(TPP) in CH$_2$Cl$_2$, which is a snow at 77 K. The latter solution showed a clear emission similar to that previously reported,[10,12] but no emission was observed from the pyridine–tetrahydrofuran solution. Absorption spectra on these solutions confirmed that the Cu^{II}(TPP) was intact.

Redox Studies. Table I summarizes redox studies on Cu, Ag, and Au porphyrins. Ag^{II} and Ag^{III} complexes show a reversible one-electron redox couple at a potential between that of the first oxidation and the first reduction of the porphyrin ring. In contrast, it has been known for some time that, with Cu^{II} porphyrin complexes, the first oxidation and reduction potentials correspond to loss and gain of electrons at the ring.[21-23] Redox studies reported here as well as the more detailed studies of Jamin and Iwamoto[16b] show that this is also true for Au^{III} porphyrins.

Near-IR Absorption. As shown above, Ag complexes, with a metal redox potential between that of ring oxidation and ring reduction, lack emission. This suggests that Ag^{II} and Ag^{III} complexes should show charge transfer (CT) absorption bands in the near IR that would be absent in complexes of either Cu^{II} or Au^{III}. These transitions should be

$$\text{Ag}^{II}, \, b_{1g}(d_{x^2-y^2}) \rightarrow e_g(\pi^*)$$

$$\text{Ag}^{III}, \, a_{1u}(\pi),a_{2u}(\pi) \rightarrow b_{1g}(d_{x^2-y^2})$$

and are forbidden. Hence their observations should require high concentration, and careful comparison between molecules with and without such absorption bands is necessary to establish their presence. Such absorption studies are shown in Figure 4.

Figure 4A compares the emitting Cu^{II}(TPP) and nonemitting Ag^{II}(TPP). It is clear that the Ag^{II}(TPP) shows much more absorption, with a clear band at ~860 nm that we at-
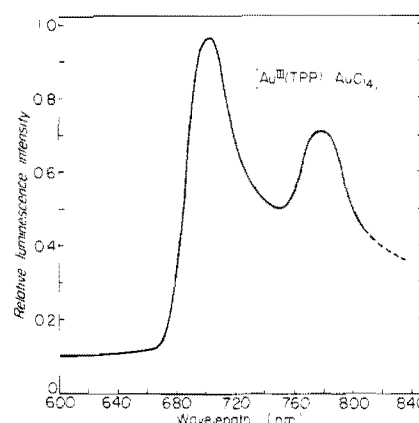
Figure 3. Luminescence spectrum of [Au^{III}(TPP)][AuCl$_4$] in a mixture of ethanol and glycerol (11:1) at 77 K. Spectrum corrected for variation of detector sensitivity with wavelength. Estimated phosphoresence quantum yield, $\Phi_p \sim 0.006$; the nonexponential decay fit with lifetimes 63 and 184 μs.

tribute to (d,π^*) charge transfer.

Figure 4B compares the emitting Cu^{II}(OEP) and the nonemitting Ag^{II}(OEP). While the Ag^{II}(OEP) shows no resolved CT band, it shows substantial absorption intensity out to 1000 nm. The Cu^{II}(OEP) shows a clear band at 682 nm that we attribute to absorption $^2S_0 \rightarrow \, ^2T_1$. This band was earlier reported in excitation spectra.[10] To longer wavelength this absorption falls off quickly where Ag^{II}(OEP) still shows substantial absorption, which we assign to (d,π^*) charge transfer transitions.

Figure 4C compares the emitting [Au^{III}(TPP)][AuCl$_4$] and the nonemitting [Ag^{III}(OEP)][PF$_6$]. While the former shows a shoulder at ~660 nm that is easily assigned to $^1S_0 \rightarrow \, ^3T_1$, the Ag^{III} complex shows IR bands at ~950 nm and also ~710-670 nm. The latter may be $^1S_0 \rightarrow \, ^3T_1$ as in the Au^{III} species. But the broad 950-nm band we attribute to (π,d) charge transfer. We have also looked at [Ag^{III}(OEP)][ClO$_4$] and its spectrum is identical with that of [Ag^{III}(OEP)][PF$_6$] given in Figure 4C.

One final comparison of interest is between Cu^{II}(TPP) and Cu^{II}(OEP). The latter shows a very clear $^2S_0 \rightarrow \, ^2T_1$ absorption peak at 682 nm; the former shows a continuously rising absorption tail with shoulders at ~713 and ~670 nm. It is perhaps in this broad tail that a (d,π^*) charge transfer absorption is hidden.

Discussion

We shall explain the experimental data with the aid of the iterative extended Hückel (IEH) calculations. As has been pointed out earlier,[3,4,7] the IEH calculations do not give correct

Figure 4. Near-infrared spectra for Cu, Ag, and Au complexes: (A) $Cu^{II}(TPP)$ (—), 1.1×10^{-3} M, and $Ag^{II}(TPP)$ (- - -), 3.8×10^{-4} M; (B) $Cu^{II}(OEP)$ (—), 1.7×10^{-3} M, and $Ag^{II}(OEP)$ (- - -), 6.8×10^{-4} M (for $Cu^{II}(OEP)$ the right part of the graph has absorbance from 1.0 to 2.0); (C) $[Au^{III}(TPP)][AuCl_4]$ (—), 5.6×10^{-4} M, $[Ag^{III}(OEP)][PF_6]$ (- - -), 3.8×10^{-4}. All in CH_2Cl_2 at room temperature in 10-cm cell. Arrows (→ or ⇢) show ϵ 50 M^{-1} cm^{-1} for each curve. Dashed curves show charge transfer absorption that quenches emission. See text.

Table II. Iterative Extended Hückel Parameters

ionization energies, eV^a	Ag	Au
IP	7.574	9.22
$M^0 \rightarrow M^+ + s$	11.08	12.17
$M^0 \rightarrow M^+ + p$	4.4	9.22
$M^0 \rightarrow M^+ + d$	17.04	15.36
IP^+	21.48	?
$M^+ \rightarrow M^{2+} + s$	17.3	18.37
$M^+ \rightarrow M^{2+} + p$	11.1	11.5
$M^+ \rightarrow M^{2+} + d$	24.8	23.12
exponents^b		
s	1.67	1.92
p	1.67	1.92
d	3.30	3.56

^{a} Based on energy levels reported in ref 25. ^{b} Exponents used for copper: 1.32 (s); 1.32 (p); 3.24 (d).

charge transfer energies, but they are useful in showing possible charge transfer transitions and their relative energies for a series of molecules calculated with a set of parameters obtained in identical manner. The parameters for the IEH calculations on Ag and Au are given in Table II; the orbital energy diagrams are given in Figures 5 and 6, where the MOs are grouped as P or M depending on whether the electron density is largely on the porphine ring or the metal atom; D_{4h} symmetry labels are used for these highest filled and lowest empty orbitals.

The Cu^{II}, Ag^{II}, and Au^{II} porphyrins (Figure 5) have a single electron in the uppermost d orbital $(d_{x^2-y^2})$. Extensive ESR studies have been done on the Cu(II) and Ag(II) porphyrins.[28-32] These studies show that there is strong σ bonding between the metal and N of the porphyrin for both Cu and Ag, the Ag σ bond being stronger. For Cu the "in-plane π bonding" of the metal d_{xy} orbitals and the ligand $N(p_x)$ or $N(p_y)$ orbitals is found to be negligible while the "out of plane π bonding" of the metal d_π with $N(p_z)$ is very small; for Ag both are small but larger than for Cu. ESR shows the metal to ring bonding to be independent of the substituents of the porphine ring. The IEH calculations are found to be in qualitative agreement with the ESR results.

For the Cu^{II}, Ag^{II}, and Au^{II} complexes the IEH calculations indicate two possible charge transfer transitions, $[a_{1u}(\pi), a_{2u}(\pi) \rightarrow b_{1g}(d_{x^2-y^2})]$ and $[b_{1g}(d_{x^2-y^2}) \rightarrow e_g(\pi^*)]$. Peel calculations done by the Swedish workers on $Cu^{II}(P)$[33] and on copper(II) phthalocyocyanine[34] indicate that the (d,π^*) transitions have lower energy, estimated to be in the visible region. Figure 5 shows that this transition decreases in energy in the order $Cu^{II}(P) > Ag^{II}(P) > Au^{II}(P)$. That the CT tran-
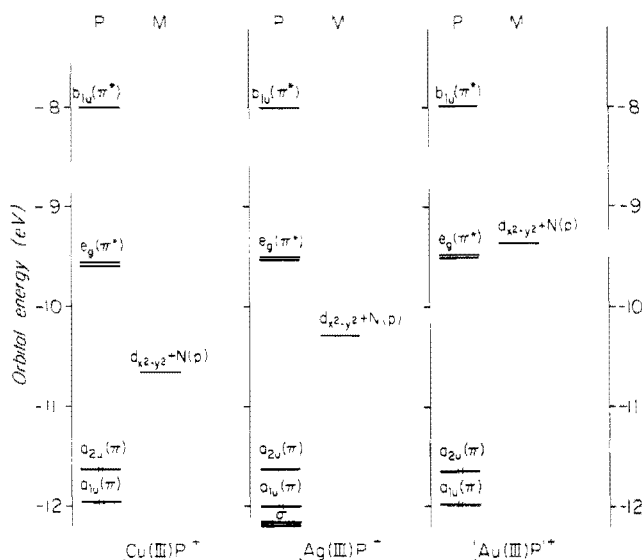

Figure 5. Energies of top filled and lowest empty MOs calculated by the iterative extended Hückel method. MOs are grouped as P or M depending on whether the electron density is largely on the porphin ring (P) or metal (M). D_{4h} symmetry labels.

sition is at highest energy in Cu^{II} but shifts to lower energy in Ag^{II} is consistent with the observed luminescence of Cu^{II} complexes, whereas Ag^{II} complexes do not emit and show near-IR absorption. The increase in energy of $d_{x^2-y^2}$ is consistent with the fact that Cu^{II} is not easily oxidizable, while Ag^{II} is, and Au^{II} is unstable. The difficulty in oxidizing to Cu^{III} also correlates with its large charge density (Table III).

Recent $X\alpha$ calculations by Case and Karplus[35] raise an important question concerning the nature of the CT states. In their intensive theoretical study of $Cu^{II}(P)$ they find that the lowest energy CT transition is (π,d) [i.e., $Cu^{I}(P^+)$] with (d,π^*) [i.e., $Cu^{III}(P^-)$] at much higher energy. This result is precisely opposite that of the Swedish Pariser–Parr–Pople calculations.[33] The IEH orbital energies (Figure 5) tend to agree with the latter but are generally unreliable for CT energy predictions. Furthermore, the $X\alpha$ studies[35] predict that reduction of $Cu^{II}(P)$ should yield $[Cu^{I}(P)]^-$ rather than $Cu^{II}(P^-)$ as inferred from redox studies (Table I). Our redox studies on $Ag^{II}(OEP)$ and $Ag^{II}(TPP)$ show no evidence for metal reduction, although the species $(Ag^{I})_2(TPP)$ has been reported.[8] The systematics of the spectra and redox properties among Cu, Ag, and Au complexes favors the conclusion that $Cu^{III}(P^-)$ is the lower energy CT state. Moreover, the quenching of the luminescence of $Cu^{II}(TPP)$ by pyridine, reported above, also indicates that the lowest energy CT state is $Cu^{III}(TPP^-)$. While the current weight of experimental evidence tends to suggest that states involving Cu^I are very high energy, further experiments on the effect of ligands on the redox potentials, infrared absorption, and luminescence, as well as picosecond studies of the CT excited state (should it live long enough), might allow definitive identification of the nature of the lowest energy CT state.

The Cu^{III}, Ag^{III}, and Au^{III} complexes (Figure 6) have an empty $d_{x^2-y^2}$ orbital; thus the possible charge transfer is $[a_{1u}(\pi), a_{2u}(\pi) \rightarrow d_{x^2-y^2}]$. The calculations show that this transition is lower for $[Ag^{III}(P)]^+$ than for $[Au^{III}(P)]^+$, again in agreement with the near-IR findings, the lack of emission for $[Ag^{III}(OEP)]^+$, and its metal redox potential. The calculations suggest that a (π,d) charge transfer transition occurs at higher energy in Au^{III} complexes. Thus it supports the assignment of the band at ~450 nm to a CT transition and the conjecture that this CT transition plays a role in the quenching of the $[Au^{III}(TPP)]^+$ emission at room temperature. Figure

Table III. Charge Densities by IEH Calculations

	$Cu^{II}(P)$	$Ag^{II}(P)$	$Au^{II}(P)$	$[Cu^{III}(P)]^+$	$[Ag^{III}(P)]^+$	$[Au^{III}(P)]^+$
metal	0.334	0.192	0.185	0.420	0.248	0.275
porphin	−0.334	−0.192	−0.185	0.580	0.752	0.725

Figure 6. Energies of top filled and lowest empty MOs calculated by the iterative extended Hückel method. MOs are grouped as P or M depending on whether the electron density is largely on the porphin ring (P) or metal (M). D_{4h} symmetry labels.

6 also suggests that the Cu^{III} complex is the most easily reduced. But the diagram fails to show why the Cu^{III} complex is unstable.

The Cu, Ag, and Au porphyrins are classified as *hypso*, i.e., blue shifted with respect to *normal* closed-shell metals;[3,4] but the blue shift is only slight. The blue shift is attributed to back-bonding repulsion between the empty $e_g(\pi^*)$ and the filled $e_g(d_\pi)$ orbitals.[3,4] In going from $Ag^{II}(OEP)$ to $[Ag^{III}(OEP)]^+$ there is a further blue shift of ~200 cm^{-1}.[18] The IEH calculations provide an interpretation of these shifts. A very low energy is calculated for $e_g(d_\pi)$ [e.g., −18.46 eV in $Ag^{II}(P)$], which is consistent with little back-bonding; thus the d_π electron density calculated for the $e_g(\pi^*)$ orbital of $Ag^{II}(P)$ is only 0.08%. This calculated d_π density changes very little in going from $Ag^{II}(P)$ to $[Ag^{III}(P)]^+$, yet the IEH energy gap between $e_g(\pi^*)$ and the average of $a_{2u}(\pi)$ and $a_{1u}(\pi)$ increases by 890 cm^{-1}, almost entirely due to a greater relative decrease in energy of $a_{2u}(\pi)$. (See Figures 5 and 6.) Thus the calculations interpret the blue shift on going from Ag^{II} to Ag^{III} porphyrin in terms of an inductive perturbation on the $a_{2u}(\pi)$ orbital due to the increased positive charge on the metal rather than to any increase in back-bonding between $e_g(\pi^*)$ and $e_g(d_\pi)$.

Summary

These studies on porphyrin complexes of Cu^{II}, Ag^{II}, Ag^{III}, and Au^{III} provide a clear explanation for the difference in their electronic structure and spectra: The $d_{x^2-y^2}$ orbital rises in energy through this series. Thus the (d,π^*) transition lies above the lowest (π,π^*) levels in Cu^{II} but below them in Ag^{II} complexes. The $d_{x^2-y^2}$ is so high in Au^{II} that the molecule is unstable. Similarly, (π,d) is above the lowest (π,π^*) levels in Au^{III} but below them in Ag^{III} complexes. The $d_{x^2-y^2}$ is so low in Cu^{III} that the molecule is unstable. This picture explains the lack of emission from Ag^{II} and Ag^{III} complexes, the low potential redox for $Ag^{II} \rightleftharpoons Ag^{III}$, and the presence in Ag complexes of near-IR absorption attributed to CT transitions. In contrast,

Cu^{II} and Au^{III} complexes show emission and lack near-IR absorption, and their first oxidation and reduction occur at the ring. The IEH calculations reported here show an increase in energy of the $d_{x^2-y^2}$ level for Cu < Ag < Au consistent with this interpretation. The quenching of emission of $Cu^{II}(OEP)$ and $[Au^{III}(TPP)]^+$ as the temperature is raised is tentatively attributed to CT transitions being thermally populated. The broadness of the emission of $Cu^{II}(TPP)$ and its quenching by pyridine can be attributed to a (d,π^*) CT transition being close to the emitting triplet state. A major difference between Pariser–Parr–Pople (PPP) calculations[33,34] and recent $X\alpha$ calculations[35] is that the former predicts that the low-energy CT transition in Cu^{II} porphyrin is (d,π^*) while the latter predicts it to be (π,d). Thus a definitive experimental determination on the nature of this state is of considerable theoretical importance.

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