of both CCP and HRP. Since proton transfer to a nearby Asp residue is possible in both proteins, it could be important in formation of an initial compound I state in both species. Since Trp 191 is absent in HRP, this state is more stable in HRP but is easily transformed to the ES complex in CCP.

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Registry No. CCP, 9029-53-2; His, 71-00-1; Trp, 73-22-3; peroxidase, 9003-99-0.

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Metal Phthalocyanine Ground States: Covalence and ab Initio Calculation of Spin and Charge Densities

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Ab initio UHFS DV–Xα calculations of the low-lying states of manganese, iron, and cobalt phthalocyanines have been carried out with basis sets corresponding to about "double-ζ" quality. Comparison with experimental spin and charge densities on β-polymorph crystals shows the ground states to be ^4E_g, ^3E_g (or less likely $^3B_{2g}$), and $^2A_{1g}$, respectively. The molecules are highly covalent, with σ donation into $3d_{x^2-y^2}$ of ca. 0.7 e and π back-donation into the macrocycle of ca. 1 e from $d_{xz,yz}$, with the other 3d orbitals fairly ionic in character. The π back-donation differs strongly between "up" and "down" spin, the up spin being mostly ionically localized in metal $3d_{xz,yz}$ orbitals whereas the down spin is strongly covalently delocalized onto the macrocycle. This large differential covalence appears in experiment as well as the calculation. Such covalence is compatible with ESR, magnetic and Mossbauer data on the crystals. Consequently, the assignment of ground state with ionic ligand field models can be misleading. The 3d dominated orbitals lie in the order $3d_{x^2-y^2} \gg 3d_{z^2} > 3d_{xy} \sim 3d_{xz,yz}$, with up-spin members lower in energy than down-spin ones, giving the observed ground states. The closeness of the $3d_{xy}$ and $3d_{xz,yz}$ down-spin orbitals in the calculation for FePc suggests that the contribution of $^3B_{2g}$ and ^3E_g in the spin–orbit mixed ground state may vary greatly depending on small changes in axial ligation. This means small changes in such ligation can produce changes in both spin and charge populations on metal and Pc of about 1 e.

Introduction

Metal complexes of tetrapyrrole ligands are widespread in biological systems and, probably concomitantly, their properties are often very sensitive to their chemical environment, both intra- and intermolecular. Metal phthalocyanines and simple porphyrins have often been used as model compounds to try to understand the details of the metal–ligand bonding in important biological molecules. In addition, metal phthalocyanines have an extensive redox chemistry with applications in electro- and photocatalytic and semiconduction processes.[1]

The compounds have a rich array of properties with complex spectra and electrochemistry, highly variable from one metal to another. The magnetic and ESR properties also cover a wide range. The first mentioned properties are broadly understood in terms of molecular orbitals models, such as iterated extended Hückel, which emphasize the covalent mixing of metal and macrocycle orbitals and the importance of charge transfer as well as intra-ring transitions.[2] On the other hand, historically, the magnetic, ESR, and related properties have been interpreted in terms of a ligand field model, with its inherently ionic basis. While such modeling has been successful in many respects, such as the explanation of the occurrence of unusual intermediate spin states, if pressed too far, inconsistent interpretation can result.[3]

Aside from the question of covalence, a further possible source of confusion is the sensitivity of ground states to intermolecular effects. For example, the ESR properties of CoPc are very different between its two polymorphs.[4] This has been recognized in the electronic spectra,[5] where attempts at a detailed understanding are restricted to weakly axially ligated solution or vapor data. In our case, we are primarily interested in the β-polymorph, so solution or vapor data bear on this only to a limited extent.

Attempts at a more fundamental understanding of the electronic structure of metal phthalocyanine free molecules by use of ab initio calculations have been made most notably by Hartree–Fock (HF),[6] Xα,[7,8] and INDO[9] methods for states of ferrous porphine, and by Xα methods for copper porphine,[7] as well as other systems.[10-15] The HF calculation shows little covalence in the metal–macrocycle bonding and takes account of electron–electron correlation by only limited configuration interaction. In contrast, the Unrestricted Xα and INDO calculations give a markedly covalent description. A beginning has been made in the proper inclusion of spin–orbit coupling for copper porphine. In these UHFS cases, and in the earlier calculation on iron and copper tetraazaporphyrin,[10] good agreement is obtained with spectroscopic, Mossbauer, and resonance data. The message to be derived from the Xα calculations is, first, covalence is important and, second, because of the energy

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Table I. Atomic Positional Coordinates Used in the Calculation (au), $z = 0.0$

	M = Co		M = Fe		M = Mn	
atom	x	y	x	y	x	y
M	0.0	0.0	0.0	0.0	0.0	0.0
N(2′)	3.626	0.0	3.642	0.0	3.663	0.0
N(1)	4.503	4.503	4.475	4.475	4.521	4.521
C(1)	5.176	2.094	5.187	2.098	5.217	2.123
C(2)	7.740	1.338	7.840	1.338	7.840	1.338
C(3)	9.989	2.721	10.089	2.721	10.089	2.721
C(4)	12.242	1.349	12.342	1.349	12.342	1.349
H(1)	9.976	4.760	10.176	4.760	10.176	4.760
H(2)	14.027	2.328	14.127	2.328	14.127	2.328

difference between up-spin and down-spin manifolds, differences in covalence between up- and down-spin molecular orbitals may be large.

Diffraction measurements of spin and charge density provide a very direct test of the ground state chosen for the calculation.[16] In that way, they provide stringent constraints on theory. However, as we have noted, theory is available only for free molecules, while experiments are on the crystals. Weak axial ligation or other intermolecular effects may cause the crystal ground state to differ from that of the free molecule. Any of the low-lying free molecule states may come to dominate in the crystal. X-ray diffraction results for the charge density in metal phthalocyanines are available for the β-polymorphs of manganese,[17] iron,[3] and cobalt[18] members, and polarized neutron diffraction (pnd) results, for the spin density in the manganese[19] and cobalt[20] cases. This makes a useful series on which to assess the success of theories. The experiments have been interpreted qualitatively[18] in terms of substantial covalence in the metal–ligand bonding, but unusual spin density features remain unexplained.

In order to provide a realistic model to aid in the qualitative interpretation of the various experiments, we have performed, using the discrete variational Xα (DV–Xα) implementation of the UHFS local density approximation method, ab initio calculations of wave functions for cobalt, iron, and manganese phthalocyanines. In simpler transition-metal complexes, such calculations seem fairly realistic,[21] and in the case of iron porphine, they apparently reproduce the observed large amount of covalence.[8] As with all calculations at this level, even for such small and simple transition-metal complexes as the $CoCl_4^{2-}$ ion, none of these theoretical methods can be expected to reproduce, nor do they reproduce, the experimental results quantitatively.[22] However, the qualitative insights produced from these wave functions prove themselves vital in interpretation of the experiments.

In the following sections, we discuss the available experimental data for the ground state electronic structure of β-MnPc, β-FePc, and β-CoPc, some aspects of the DV–Xα method as applied to these systems, the results of our calculations, and finally, the use of our calculations in the interpretation of the experiments. This shows that a simple chemical model of bonding is supported by theory and provides an excellent qualitative model even for a system so large, and so delicately balanced electronically, as the phthalocyanines.

Previous Experiments and Interpretation

Structure. The structures of β-CoPc and β-MnPc have been determined at liquid-helium temperature by neutron diffraction[23,24] and also, along with β-FePc, at liquid-nitrogen temperature by X-ray diffraction.[3,17,18] The general structural features of the molecules, idealized to D_{4h} symmetry, are illustrated in Figure 1. In the crystals, they depart slightly from planar symmetry, and the 4-fold axis is not present, but the deviations, even though significant, are small. We use a coordinate system for the metal atom with z perpendicular to the molecular plane and x and y pointing at the coordinated N(2) and N(2′) atoms respectively. The coordinates used in the calculations, idealized to D_{4h} symmetry, and reconciled between molecules, are given in Table I.

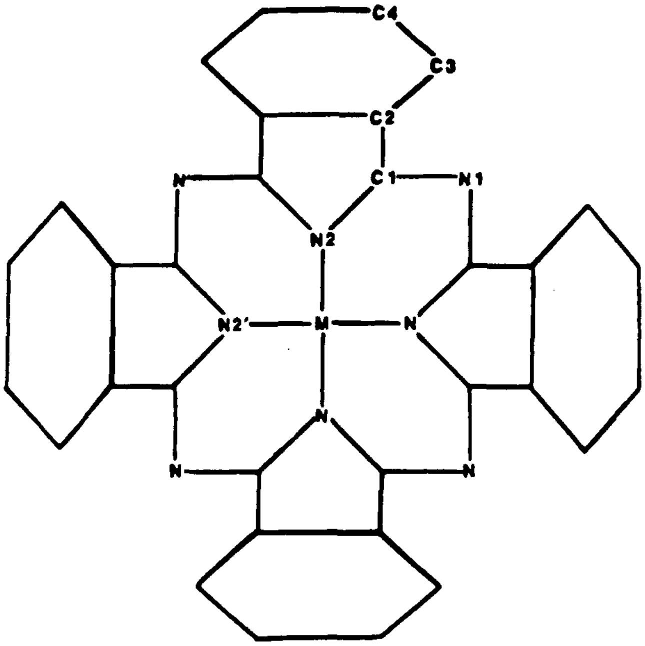

Figure 1. Numbering of the non-hydrogen atoms in the $M^{II}Pc$ molecules, idealized to D_{4h} symmetry H(1) is attached to C(3) and H(2) and C(4).

3d Ionic Electron Configurations. Charge-transfer bands in the optical spectra of metal phthalocyanines indicate that these molecules are members of an extensive redox series that can be roughly formulated as $M^{2+}Pc^{2-}$.[25] Unfortunately, in the spectrum of CoPc, charge-transfer bands obscure the the 3d–3d transitions, but inelastic electron-tunneling spectroscopy on the compound indicates that a band of 3d levels all lie very close in energy in between the mainly Pc HOMO and LUMO.[26] In addition there are weak charge transfer bands also indicating 3d levels between HOMO and LUMO.[2,25,27] The observation of these bands also probably implies covalent interaction between $3d_\pi$ and π orbitals of the metal-free macrocycle.

The electronic structures of metal(II) tetrapyrroles, particularly the metal 3d configuration, are known to be very sensitive to their chemical environment.[28] A direct illustration of this fact is the quite different 3d configurations observed by X-ray diffraction in FePc[3] and in (*meso*-tetraphenylporphinato)iron,[29] where both molecules have quite similar ligand environments around the iron(II) atoms. Such observations have possible biochemical implications. However, for the present purposes, we restrict ourselves to considering $M^{II}Pc$ experiments on the β-polymorphs only.

(a) Cobalt Phthalocyanine (CoPc). The magnetic susceptibility of β-CoPc[30] defines a low-spin $S = {}^1/_2$ ground state, with the $3d_{x^2-y^2}$

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orbital well above the other four 3d orbitals in energy. The ESR **g** tensor is very anisotropic,[31] again indicating a square-planar coordination around Co[32] and $3d_{x^2-y^2}$ well separated above the other 3d orbitals. Those results can be accounted for with the fundamentally ionic ligand field model,[28] which involves a spin-paired orbital description. Sontum et al. point out that spin-unrestricted interpretations of such observations may well be much simpler. We shall see later that is indeed so on the basis of our calculation. The ligand field model gives the ground state as mainly the $^2A_{1g}$, $3d_{xz,yz}{}^4 3d_{xy}{}^2 3d_{z^2}$.[1] However substantial participation of the ^2E, $3d_{xz,yz}{}^3 d_{xy}{}^2 3d_{z^2}{}^2$, and perhaps other quartet states is found, having been mixed in by spin–orbit coupling. The spectroscopy and ESR spectroscopy of related cobalt(II) square-planar molecules where charge transfer does not obscure the d–d bands[33] has been interpreted as showing that the spin can reside mainly in either the $3d_{z^2}$ or the $3d_{xz,yz}$ orbitals, fine details determining which. The $^2A_{1g}$ and ^2E term energies are seen to be very close and either could be the lower, depending on small changes in the environment of the cobalt atom. The large change in the **g** tensor from the α- to the β-polymorph[34] indicates that there are substantial intermolecular effects giving some effective axial ligation. This axial ligation is also indicated by the decrease in symmetry from D_{4h} noticed in the X-ray structure. Nevertheless, the large tetragonal ligand component still dominates in β-CoPc.

The observed temperature dependence of the magnetic susceptibility[35] is not simple, but it also is explained by the above models.[36] At low temperatures, the magnetic moment is that expected from a **g** tensor arising from a dominant $3d_{z^2}$ configuration with large participation from $3d_{xz,yz}$. At higher temperatures, a temperature-independent paramagnetic term becomes important. It probably arises from interaction with a low-lying excited state dominated by the $3d_{xz,yz}$ configuration. All these experiments support a self-consistent model of a spin $^1/_2$ ground state dominated by $3d_{z^2}$ with some $3d_{xz,yz}$ participation.

(b) Iron Phthalocyanine. The magnetic behavior of β-FePc[38-40] at higher temperatures indicates an intermediate spin ground state, $S = 1$, which is orbitally nondegenerate but has some orbital angular momentum mixed in from the low-lying ^3E_g state. However, the fit to the data is less than satisfying.[41] A large zfs of ca. 65 cm^{-1}, with $m_s = 0$ as the ground state, fits the lower temperature magnetic susceptibility experiments. Mossbauer studies[42,43] indicate that the electric field gradient at the iron nucleus corresponds to a prolate ellipsoidal charge density. Within a ligand field model this seems to support the ^3E_g ground state, but an ad hoc introduction of covalence makes that conclusion less certain.

(c) Manganese Phthalocyanine. The magnetic behavior of β-MnPc[4] is complicated by appreciable intermolecular ferromagnetic exchange, but the magnetic susceptibility and magnetization data at higher temperatures[44,45] are moderately anisotropic and indicate a quartet spin state in which some excited ^4E_g term is mixed by spin–orbit coupling into a $^4A_{2g}$ or $^4B_{2g}$ ground state. Within an angular overlap ligand field model, only a $^4A_{2g}$ ground state satisfies the data with reasonable values for parameters,[19] and it gives the configuration $3d_{xy}{}^2 3d_{xz,yz}{}^2 3d_{z^2}{}^1$ and a zero-field splitting (zfs) of ca. 40 cm^{-1}. However, some doubt remains about the interpretation. In order to obtain the low temperature magnetic structure which is observed in the pnd experiment,[19] the model of Miyoshi[37] requires a large negative D parameter in the ESR spin Hamiltonian, in addition to the ferromagnetic exchange, and that is not compatible with some of the magnetic susceptibility data at higher temperatures.

Covalent Interactions. The above explanations of the physical properties of the β-metal phthalocyanines are complicated by covalence. Already ESR orbital reduction factors,[46] IR and structural data on related compounds,[47] and MCD spectra[48] have indicated large covalent effects that must render the ligand field model unrealistic. The charge and spin density data show clear evidence of both covalence and electron correlation effects. For example, the 3d configurations actually observed bear little relationship to free-ion-based possibilities. Thus in FePc the $3d_{z^2}$ and $3d_{xz,yz}$ charge populations of 0.93 (6) and 2.12 (7) e^3 do not match any of the ionic model configurations (1, 3; 2, 2; 1, 4; or 2, 3 e), and again the spin in the 3d orbitals of CoPc and MnPc[19,20] is substantially larger than for an ionic model (1.43 (5) and 3.76 (6) e versus 1 and 3 e).

Since the charge and spin density data for CoPc have been discussed in detail[18] we will only summarize the conclusions here. From the pnd results, we see that in the ground state the following observations may be made:

(1) The 3d configuration, with the orbital correction of Barnes, Chandler, and Figgis[49] shows a substantial admixture of $3d_{xz,yz}$ orbitals—viz. $3d_{z^2}{}^{0.88(13)} 3d_{xz,yz}{}^{0.78(22)}$—which is incompatible with any ionic ground state and is not obviously explicable.

(2) Negative spin (−0.16 (5) e) is found on the macrocycle, and that can only arise through spin polarization, a facet of electron–electron correlation, within rather covalent molecular orbitals.

(3) Negative (down) spin in cobalt $3d_{x^2-y^2}$ and diffuse "4p" functions is further evidence of electron correlation.

The X-ray diffraction results, when revised to include an improved, anharmonic, model of thermal motion,[50] show a cobalt atom configuration of $3d_{xz,yz}{}^{2.88(5)} 3d_{xy}{}^{1.67(4)} 3d_{z^2}{}^{1.32(4)} 3d_{x^2-y^2}{}^{0.51(4)}$-$4p^{0.74(15)}$. Together with the Pc populations a consistent interpretation is as follows: (1) a covalent σ donation of 0.51 (4) e from nitrogen lone pairs into the $3d_{x^2-y^2}$ orbital; (2) in-plane covalent π back-donation of 0.33 (4) e and out-of-plane 1.12 (5) e π back-donation into the Pc and the diffuse region between cobalt and it; (3) transfer of 0.32 (4) e to $3d_{z^2}$.

Comparison of the spin and charge density results shows that spin polarization must be invoked to make the experiments consistent with each other. The diffraction experiments on CoPc include much detail on the ground state, and our interpretation requires the effects of electron correlation and of σ and π covalence. The diffraction results for FePc and MnPc have not been analyzed in such depth, but they also show many of the qualitative features observed in CoPc.[18]

The features outlined above are not simple to model, so examination of reasonably good theoretical wave functions of appropriately selected ground states may aid in the interpretation.

Discrete-Variational Xα Method

The DV-Xα method has been used over a wide area of chemistry (see for example applications to Pc compounds[4,51,52]) so we

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present only an outline here. DV–Xα calculations of the wave function for a molecule, as currently implemented by Ellis et al., require only two assumptions. First, the nonlocal exchange-correlation term can be replaced by the local Hartree–Fock–Slater term in calculation of the local density, the fundamental object of the theory.[53] Second, the use of the local density orbitals in a single determinant unconstrained wave function gives a realistic many-body wave function. Because it employs numerical rather than analytic basis sets, with sufficient integration points, and with sufficient multipoles used in the fitting of the potential, the only serious remaining error lies in the quality of the basis set.[54]

We have employed here as basis sets a single numerical function per valence orbital, obtained by numerical solution of the HFS equations for the atoms or ions. However these numerical atomic functions, while accurate for the atoms, are not sufficiently flexible for molecular calculations of the highest accuracy. An improvement, which we use, is to solve the molecular wave function by using the ionic basis functions. Then we perform a second calculation, this time using as basis functions those derived from atomic solutions by using the Mulliken populations of the initial molecular calculations. Further iteration is not necessary as the Mulliken populations of the second calculation are very close (within 0.05 e) of the basis calculation.

For the M(II) atoms we use functions 1s–4p, for C and N, 1s–2p, and for H, 1s. This is an almost minimal basis set for the DV–Xα method, but corresponds to quite high-quality sets for conventional HF or UHF calculations based on Gaussian functions. The atomic cores (M(II) 1s–3p; C and N 1s) were frozen in the calculation. A total of 9000 integration points were employed, an adequate number to give negligible numerical errors. The molecular Coulomb potentials were fitted were multipoles up to order 1 on C and N, and of order 2 on the metal atom, which has been found adequate even with bases involving d functions.[54]

Metal Phthalocyanine Wave Functions—Results

We will discuss the calculations on CoPc in some detail, followed by the essential matters for MnPc and FePc, since in broad outline all the calculations are similar.

The ground state found here for CoPc is $^2A_{1g}$. In Table II a list of eigenvalues from −13.08 to −4.09 eV, which encompasses all the orbitals with significant cobalt 3d Pc bonding, is given. A list of the eigenvalues near the Fermi level, with notes on the associated eigenvector, are given in Table IIb for all occupied orbitals with cobalt coefficient >0.2, and also unoccupied ones with 3d coefficient >0.2. We notice that 4p participation in e_u MO's is small and is not concentrated in any particular orbital, while 4s in a_{1g} is larger, and it mixes noticeably with $3d_{z^2}$. In Table III we show Mulliken populations for the cobalt orbitals in CoPc for three possible ground states.

We have performed two further calculations on CoPc. A RHFS calculation, with all other factors unchanged, gives the same ground state, $^2A_{1g}$, with a very similar charge distribution to the unrestricted calculation. The amount of covalent charge transfers are about 80–90% of the unrestricted values. The spin distribution is, of course very different, with ca. 0.92 spin in $3d_{z^2}$ and zero in the other 3d orbitals. A further calculation with 3d polarization basis functions added to all the carbon and nitrogen basis functions also gave the same ground state. The covalent charge transfers were increased from the smaller basis calculation by about 10% with the crucial exception of the e_g down-spin orbitals where it was reduced by almost 40%. This shows that the π bonding is very sensitive to basis set, and therefore difficult to calculate correctly. A further difficulty is our complete neglect of the presumably small but, as we shall see, important axial ligation effects. We report the results from the basis without 3d functions on C and N, since they agree better with the diffraction results and they enable us to make comparisons with our calculations on the other two compounds. Our object is to understand the diffraction results, and for this qualitative results from the theory are sufficient.

Table II

(a) Eigenvalues for Molecular Orbitals between −13.08 and −4.09 eV for CoPc

up spin, g		down spin, g	up spin, u		down spin, u
−13.079	$8b_{1g}$	−13.007	−12.995	$13e_u$	−13.006
−12.793	$6b_{2g}$	−12.801	−12.764	$14e_u$	−12.773
−12.747	$6a_{2g}$	−12.756	−12.514	$1b_{2u}$	−12.548
−12.687	$9a_{1g}$	−12.626	−11.798	$1b_{1u}$	−11.836
−12.048	$9b_{1g}$	−11.836	−11.329	$15e_u$	−11.340
−11.355	$7b_{2g}$	−11.364	−11.241	$16e_u$	−11.229
−11.298	$7a_{2g}$	−11.310	−10.831	$17e_u$	−10.841
−10.950	$2e_g$	−10.969	−10.769	$2a_{2u}$	−10.780
−10.910	$10a_{1g}$	−10.919	−10.442	$2b_{2u}$	−10.461
−10.757	$10b_{1g}$	−10.763	−9.239	$1a_{1u}$	−9.272
−10.438	$3e_g$	−10.363	−8.996	$18e_u$	−9.011
−9.519	$11a_{1g}$	−9.532	−8.894	$3a_{2u}$	−8.896
−9.104	$4e_g$	−8.670	−8.467	$2b_{1u}$	−8.481
−8.980	$8b_{2g}$	−8.787	−8.417	$4a_{2u}$	−8.427
−8.458	$5e_g$	−8.467	−8.338	$3b_{2u}$	−8.352
−8.463	$12a_{1g}$	-6.454^a	−7.362	$2a_{1u}$	−7.409
−8.050	$9b_{2g}$	−7.082	-4.612^a	$3b_{1u}$	-4.635^a
−7.920	$6e_g$	−6.867	-4.108^a	$4b_{2u}$	-4.144^a
-5.988^a	$7e_g$	-5.833^a			
-4.997^a	$11b_{1g}$	-4.089^a			

(b) CoPc Molecular Orbitals with Calculated Cobalt 3d Participation

orbital	spin	energy, eV	cobalt coeff
		Occupied	
$8b_{1g}$	+	−13.079	0.28 $3d_{x^2-y^2}$
$8b_{1g}$	−	−13.007	0.20 $3d_{x^2-y^2}$
$9b_{1g}$	+	−12.048	0.43 $3d_{x^2-y^2}$
$9b_{1g}$	−	−11.816	0.41 $3d_{x^2-y^2}$
$3e_g$	+	−10.438	0.32 $3d_{xz,yz}$
$4e_g$	+	−9.104	0.67 $3d_{xz,yz}$
$8b_{2g}$	+	−8.980	0.59 $3d_{xy}$
$8b_{2g}$	−	−8.787	0.26 $3d_{xy}$
$4e_g$	−	−8.670	0.30 $3d_{xz,yz}$
$12a_{1g}$	+	−8.463	0.95 $3d_{z^2}$, −0.22 4s
$9b_{2g}$	+	−8.050	0.80 $3d_{xy}$
$6e_g$	+	−7.920	0.62 $3d_{xz,yz}$
$9b_{2g}$	−	−7.082	0.96 $3d_{xy}$
$6e_g$	−	−6.867	0.77 $3d_{xz,yz}$
		unoccupied	
$12a_{1g}$	−	−6.453	0.96 $3d_{z^2}$, −0.23 4s
$7e_g$	+	−5.988	0.20 $3d_{xz,yz}$
$7e_g$	−	−5.833	0.50 $3d_{xz,yz}$
$11b_{1g}$	+	−4.997	0.87 $3d_{x^2-y^2}$
$11b_{1g}$	−	−4.089	0.91 $3d_{x^2-y^2}$

[a] Virtual, unoccupied orbital.

In Table III, we also show the results for FePc in forms that are exactly comparable with those for CoPc and MnPc. For FePc we find a $^3B_{2g}$ ground state, and for MnPc a ^4E_g ground state. The calculation for FePc was difficult to converge, as it tended to oscillation between ^3E_g and $^3B_{2g}$ ground states, which are very close in calculated energy. The energy difference was estimated by a transition-state calculation. The calculations all stabilized at almost the same pair of states, which we use in this paper. In addition, we performed a calculation omitting the l = 1 and 2 multipoles in the charge fit (thus giving the self-consistent charge, SCC, version of the DV–Xα procedure), and also included a number of transition-state calculations to estimate energy differences between the states.[53] Table IV shows eigenvalues around the Fermi level for the likely ground states of the three compounds. We list the major 3d molecular orbitals plus everything between $2a_{1u}$ and $7e_g$, which includes all the levels involved in the Q-band optical spectrum. Table V shows spin populations on the macrocycle in more detail. Selected transition-state calculations for the state energies relative to the ground state show, as expected, that where mainly the 3d configuration is changed both the state energy difference and excited-state orbital populations are given by the ground-state orbitals (including the appropriate virtual

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Table III. Selected Mulliken Populations for M–Pc Bonding (M = Co, Mn, Fe) Compared with Experimental Least-Squares Populations

CoPc

	^2E_g		$^2B_{2g}$		$^2A_{1g}$				experiment[18,20]			
	charge	spin	charge	spin	charge	spin	up spin	down spin	charge	spin	up spin	down spin
$3d_{x^2-y^2}$	0.708	0.076	0.708	0.076	0.708	0.076	0.392	0.316	0.51 (4)	−0.27 (12)	0.12 (6)	0.39 (6)
$3d_{xy}$	1.968	0.004	1.047	0.925	1.968	0.004	0.986	0.982	1.67 (4)	0.04 (12)	0.86 (6)	0.81 (6)
$3d_{xz,yz}$	2.785	1.000	3.382	0.438	3.382	0.438	1.910	1.472	2.88 (5)	0.78 (22)	1.83 (11)	1.05 (11)
$3d_{z^2}$	1.947	−0.006	1.947	−0.006	1.028	0.913	0.971	0.057	1.32 (4)	0.88 (13)	1.10 (7)	0.22 (7)
tot. 3d	7.408	1.074	7.084	1.433	7.087	1.432	4.259	2.827	6.38 (6)	1.43 (5)	3.91 (4)	2.48 (4)
tot. 4 s/p	0.401	0.050	0.401	0.050	0.346	0.105	0.292	0.169	0.74 (15)	−0.27 (9)	0.24 (9)	0.51 (9)
tot. Pc charge/spin	−1.191	−0.124	−1.515	−0.483	−1.567	−0.537	...	...	−1.88 (16)	−0.17 (5)	...	...
goodness of fit (χ^2)	248	57	613	113	233	17						

FePc

	$^3A_{1g}$		^3E_g		^3E_g		$^3B_{2g}$		experiment[3]	
	charge	spin	charge	spin	charge	spin	charge	spin	charge	spin
$3d_{x^2-y^2}$	0.805	0.171	0.675	0.143	0.805	0.171	0.675	0.143	0.70 (7)	...
$3d_{xy}$	1.970	0.008	1.031	0.940	1.970	0.008	0.031	0.940	1.68 (10)	...
$3d_{xz,yz}$	2.641	1.265	2.335	1.467	2.903	1.003	2.579	1.205	2.12 (7)	...
$3d_{z^2}$	1.946	−0.001	1.928	0.006	1.035	0.910	1.017	0.917	0.93 (6)	...
tot. 3d	7.362	1.443	5.969	2.556	6.712	2.093	5.320	3.204	5.42 (6)	...
tot. 4 s/p	0.433	0.078	0.388	0.075	0.361	0.150	0.326	0.147	0.0 fix	...
tot. Pc charge/spin	−0.205	0.479	−1.643	−0.631	−0.927	−0.243	−2.364	−1.351	−2.58 (6)	
goodness of fix (χ^2)	349	...	330	...	138	...	87	...		

MnPc

	$^4A_{1g}$		$^4B_{2g}$		^4E_g		experiment[17,19]	
	charge	spin	charge	spin	charge	spin	charge	spin
$3d_{x^2-y^2}$	0.730	0.216	0.730	0.216	0.730	0.216	0.1 (2)	−0.13 (4)
$3d_{xy}$	1.026	0.948	1.981	−0.007	1.026	0.948	1.5 (2)	0.88 (4)
$3d_{xz,yz}$	2.061	1.784	2.061	1.784	2.189	1.656	1.3 (3)	2.05 (4)
$3d_{z^2}$	1.922	0.012	1.018	0.916	1.018	0.916	0.9 (1)	0.95 (4)
tot. 3d	5.739	2.960	5.790	2.909	4.963	3.736	3.8 (2)	3.75 (5)
tot. 4 s/p	0.389	−0.275	0.309	−0.195	0.309	−0.195	2.0 (3)	−0.40 (4)
tot. Pc charge/spin	−0.872	0.315	−0.901	0.286	−1.728	−0.931	−1.2 (3)	−0.36 (4)
goodness of fit (χ^2)	126	645	24	569	26	171		

Table IV. Eigenvalues for CoPc, FePc and MnPc, Close to the Fermi Level

		energy, eV			
orbital	approx nature	CoPc ($^2A_{1g}$)	FePc (^3E_g)	FePc ($^3B_{2g}$)	MnPc (^4E_g)
$2a_{1u}$-	lig	−7.41	−7.21	−7.21	−7.20
$2a_{1u}$+	lig	−7.36	−7.16	−7.16	−7.16
$9b_{2g}$-	$3d_{xy}$	−7.08	−7.17	−5.92[b]	−5.55[b]
$6e_g$-	some $3d_{xz,yz}$ +lig	−6.87	−6.86[a]	−6.22	−6.14[a]
$12a_{1g}$-	$3d_{z^2}$	−6.45[b]	6.53[b]	−5.26[b]	−4.66[b]
$7e_g$+	lig	−5.99[b]	−5.76[b]	−5.69[b]	−5.75[b]
$7e_g$-	some $3d_{xz,yz}$ +lig	−5.83[b]	−5.61[b]	−5.06[b]	−4.69[b]
$11b_{1g}$+	$3d_{x^2-y^2}$	−4.99[b]	−5.84[b]	−4.82[b]	−5.06[b]
$11b_{1g}$-	$3d_{x^2-y^2}$	−4.09[b]	−4.03[b]	−2.91[b]	−2.34[b]

[a] Half-occupied. [b] Unoccupied.

ones). Where charge transfer to the macrocycle is involved there is, again as expected, significant orbital relaxation, changing energy differences by up to 50%, with noticeable MO eigenvector changes. Since we are concerned with ground-state choices involving differing metal 3d populations, not spectroscopy involving charge transfer, we do not report these calculations in more detail here.

Metal Phthalocyanine Wave Functions—Discussion

Covalence. The u-type orbitals play little part in the bonding, as is shown by the low metal coefficients in the MO's and, indirectly, by the small splitting of up- and down-spin pairs of metal-free Pc molecular orbitals.

In contrast, the g-type orbitals can show very large amounts of covalence. Metal-free Pc has two orbitals close to the Fermi level, well adapted for covalent bonding to a metal atom—the filled b_{1g} N(2) lone-pair MO and an empty π^*e_g orbital. Consequently the orbitals containing $3d_{xy}$ and $3d_{z^2}$, b_{2g} and a_{1g}, show little spin and charge transfer since the metal orbitals participate in no suitable Pc MO. In contrast, orbitals containing $3d_{x^2-y^2}$, viz. b_{1g}, show substantial σ charge transfer to the metal since the empty 3d orbital interacts with filled N(2) lone pairs. The $3d_{xz,yz}$ e_g (d_π) orbitals show the effects of interaction between filled 3d and empty Pc π^* orbitals, which result in strong π back-donation onto the macrocycle. While this explains the main features, other weaker effects are also important. Although weak, σ bonding involving the $3d_{z^2}$ orbital is large enough to increase its energy above that

Table V. Pc Spin Populations, Calculated and Observed, for M^{II}Pc Compounds

	CoPc ($^2A_{1g}$)		FePc (^3E_g)	FePc ($^3B_{2g}$)	MnPc (^4E_g)	
	calc	obs	calc	calc	calc	obs
N(2)	−0.014	0.003 (10)	−0.045	−0.076	−0.115	−0.032 (4)
C(1)	−0.040	−0.024 (10)	−0.019	−0.077	−0.032	−0.014 (3)
N(3)	−0.003	−0.014 (4)	0.002	−0.031	−0.027	−0.021 (4)
C(2)	−0.003		0.007	−0.010	−0.000	−0.004 (3)
C(3)	−0.009		−0.002	−0.015	−0.007	
C(4)	−0.008		−0.004	−0.015	−0.004	
H(1)	0.001		0.001	0.001	0.001	
H(2)	0.001		0.001	0.001	0.000	

of the π orbitals in all the compounds.

The effect of correlation is revealed in the energy splittings of orbital pairs of up and down spin, as those with up spin generally have a lower energy than those with down spin. Due to their improved energy matching with available empty π^* Pc orbitals, this generally causes more covalence in down-spin than in the up-spin MO's. That in turn then results in the leakage of down spin onto the Pc through covalence. This is most marked for $3d_{xz,yz}$ e_g orbitals, for which the net effect is a very distinct spin transfer of down spin onto Pc. The relevant MO, $6e_g$-, is most metal-centered for CoPc (3d coefficient 0.77), intermediately (0.51) for FePc, and least (0.36) for MnPc. An alternative way of looking at this is to say that, within a RHF framework, there is a large configuration interaction admixture. For CoPc, for example, a $t_{2g}{}^5e_g{}^1$ Pc^{1-} configuration with two up spins on the cobalt atom and one down spin on Pc is mixed into the $t_{2g}{}^6eg^1Pc^{2-}$ ground state. This "accidental" near degeneracy coupled with the naturally arising differential effect of the spin covalence combines to make the calculated spin and charge transfers rather unusual in this system and particularly sensitive to the precise method of calculating the wavefunction.

Theoretical Ground States. For all the three metal phthalocyanines considered here we get the same ordering of the energies of the 3d-dominated MO's, $3d_{x^2-y^2} \gg 3d_{x^2} > 3d_{xy} \cong 3d_{xz,yz}$, as seen from Table IV. Thus for the $3d^5$ ion (Mn) we predict a spin quartet, for $3d^6$ a triplet, and for $3d^7$ a doublet, due to the inaccessibility of the b_{1g} $3d_{x^2-y^2}$ orbital. These results are well-known from experiment. We also predict a singly occupied a_{1g} d_z2 orbital in all cases. This large splitting of a_{1g} from the remaining 3d orbitals is smaller if we use a SCC form of the calculation. It seems an aspherical local Coulomb charge fit is an important feature of the calculation.

Whether the b_{2g} ($3d_{xy}$) or the e_g ($3d_{xz,yz}$) orbitals are the last to be filled changes from MnPc to CoPc. For MnPc, we calculate a ^4E_g ground state, that is, for the free ion, the $3d_{xy}{}^1 3d_{xy,yz}{}^3 3d_{z^2}{}^1$ configuration where the last electron occupies e_g. In contrast, for CoPc, we predict a $^2A_{1g}$ ($3d_{xy}{}^2 3d_{xz,yz}{}^4 3d_{z^2}{}^1$) ground state with the last electron in b_{2g}. For FePc, we find near degeneracy: $^3B_{2g}$ ($3d_{xy}{}^1 3d_{xz,yz}{}^4 3d_{z^2}{}^1$) is calculated as the ground state but ^3E_g ($3d_{xy}{}^2 3d_{xz,yz}{}^3 3d_{z^2}{}^1$) lies only 0.003 eV (24 cm^{-1}) above it, with the other $^3A_{1g}$ and ^3E_g states corresponding to other configurations much higher. These observations can be rationalized by noting that while b_{2g} ($3d_{xy}$) remains ionic, there is a steady trend in the $6e_g$- orbital containing $3d_{xz}$, which puts more charge on the Pc, corresponding to more covalency and lower energy with respect to b_{2g}.

We may also take spin–orbit coupling into account, as a perturbation within the 3d components of the MO's. The 3d populations for MnPc and CoPc should remain close to that predicted above for the ^4E_g and $^2A_{1g}$ covalent wave functions, but due to the near degeneracy, it is possible that for the FePc $^3B_{2g}$ and ^3E_g terms substantial spin–orbit mixing may occur to give some intermediate population, for the ground state and possible thermal population of all resulting states.

Other related calculations have given ground states with a_{1g} more highly occupied. For example, a $^3A_{2g}$ ground term has been deduced for ferrous porphine. The $X\alpha$ muffin-tin calculations of Sontum et al.,[8] because of the spherical potential near the iron atom, depress a_{1g} and favor its occupation in square-planar complexes. Sontum et al. discuss this error, and Edwards et al. demonstrate its importance for $Pt(CN)_4{}^{2-}$. Other calculations, even the very extensive RHF–CI calculations of Rohmer,[6] still do not include the correlation adequately, particularly the orbital relaxation necessary to describe each individual state.[9]

Since we are interested in describing the β-polymorph experimental ground states, all these calculations including covalence and correlation may be useful.

Comparison with Experiment

Spin and Charge Densities. When we compare the theoretical Mulliken populations with the populations obtained by least-squares refinements from experiment (Table III) there is a qualitative agreement, in both spin and charge parameters for the calculated ground states. The calculated excited states give poorer fits, confirming the nature of the ground states. As a rough figure of merit we tabulate the goodness of fit (χ^2) between the four experimental theoretical 3d populations. Although this suppresses some information, such as spin on Pc, this measure also favors the assigned crystal ground states. The experimental conclusions listed in the introduction are also reported by the theoretical wave function. In particular, we see in the spin experiments the very low $3d_{xz,yz}$ down-spin population in e_{g-}, resulting from the generally greater covalence in down-spin than up-spin MO's.

For CoPc, the near-unit spin observed in $3d_{z^2}$, confirms the ground state as mainly $^2A_{1g}$. The large $3d_{xz,yz}$ spin population is seen to arise because of the much greater delocalization of e_g down spin than of up spin, which is a spin-polarization effect. A $^2B_{2g}$ ground state is not compatible with experiment, because the $3d_{xy}$ population is observed as almost zero, not 0.925, nor is ^2E_g, because of not only the low $3d_{z^2}$ population but also the low total spin population in 3d orbitals. The 3d charge density populations strengthen the conclusion, particularly the $3d_{z^2}$ population, and $3d_{xy}$ being larger than $3d_{z^2}$. In the light of the theoretical calculation, we now see that the very low $3d_{xz,yz}$ population, 2.88 rather than 4.0 e for an ionic formulation, is a manifestation of the strong π covalence. The spin distribution calculated on the Pc fragment is negative, −0.17 (5) (down), as observed. The theory predicts little interaction with the benzene rings, again as observed. Quantitatively we see that the calculated covalence for the e_g-orbital, although large, is still a good deal smaller than found from experiment. Possible explanations are incompleteness of our basis sets, the inadequacy of the UHF treatment in giving an account of electron–electron correlation, and intermolecular and/or axial ligation effects.

For FePc, we do not have pnd spin density information because, due to the large zero-field splitting, sufficient magnetization cannot be obtained experimentally. However, from the charge density study, $^3A_{1g}$ and one of the ^3E_g ground terms seem unlikely as they would have almost 2.0 e in $3d_{z^2}$. The low total 3d population and high ring charge point toward the $^3B_{2g}$ ground state, with two down-spin electrons (ionic formulation $3d_{xz,yz}$) mostly delocalized onto Pc. However, the high $3d_{xy}$ population indicates a doubly occupied state, that is ^3E_g. We have noticed already in CoPc that the calculations underestimate the π delocalization from $3d_{xz,yz}$ and that there $3d_{xy}$ has an observed population of 1.67 (4) e. These comparisons make it more probable the FePc ground state is ^3E_g, with a high degree of delocalization away from the iron atom. However, given the errors in the calculation and the lack of spin data, we cannot definitely discriminate between the two states.

We also see quite a change in π covalence between the states. ^3E_g is almost ionic in the $3d_{xz,yz}$ down-spin orbitals (population = 0.950, ionic 1.0 e) whereas $^3B_{2g}$ is quite covalent (population = 0.696, ionic 2.0 e). If there are indeed two FePc states close in energy, but very different in covalence and spin and charge delocalization onto Pc, we might expect small changes in ligation to the iron atom may have considerable influence on spin and charge densities and so produce large magnetic and other property changes for quite small chemical changes.

For MnPc, the large observed $3d_{z^2}$ spin population removes $^4A_{2g}$ as a major contributor to the ground state, while the large $3d_{xy}$ population removes $^4B_{2g}$. The approximate equality observed in those two populations and the greater $3d_{xz,yz}$ population are exactly as expected from the ^4E_g ground term. The charge experiment is compatible with this, and the $3d_{z^2}$ population eliminates $^4B_{1g}$ as a large contributor to the ground state. The low total 3d charge again supports ^4E_g. A further confirmation is the large observed and calculated π populations on N(2). Again the theory seems to underestimate the amount of covalence.

In all three crystals, we notice that $3d_{z^2}$ is preferentially unoccupied. This may well be because of weak σ axial ligation in the β polymorph crystal. In the vapor phase, or in a very weakly ligating solvent, such as dichlorobenzene, this level is less disfavored and may become accessible, as some other theoretical calculations suggest.

Magnetic Susceptibility, ESR, and Spectroscopic Results. In the light of the highly covalent wave functions that we see pertain for the metal phthalocyanines, ionic type ligand field interpretations of magnetic susceptibility, ESR, and other physical properties of the molecules are liable to be misleading. For CoPc the primary feature of the ESR spectrum, the large g tensor anisotropy, has previously been interpreted as the CI mixing of a $3d^7\ {}^2E_g$ state into the ground $3d^7\ {}^2A_{1g}$ term. We now see that this is a covalent, charge-transfer effect and should not be fitted to an ionic model. Our ground ${}^2A_{1g}$ state has substantial 3d orbital moment due to the unpaired spin in $3d_{xz,yz}$ arising from spin polarization, which gives large anisotropy in the g tensor. Similarly for MnPc, the ${}^4E_g$ state, given the large reduction in down spin in $3d_{xz,yz}$ from 1 e to almost zero, resembles an orbitally nondegenerate state into which only a small amount of orbital moment has been mixed. Last, for FePc, with its probable ${}^3E_{2g}$ ground state, some 3d orbital angular momentum introduced via delocalization of the down spin in $6e_g$- again explains qualitatively the magnetic susceptibility and anisotropy. As far as the Mossbauer data are concerned, the covalent increase in $3d_{x^2-y^2}$ population renders the ionic 3d distribution more prolate, as Dale[45] has pointed out. The present calculations show that the reduction in $3d_{xz,yz}$ population is also very important in rendering the 3d distribution more prolate, as required experimentally. Coppens and Li[3] have already demonstrated that the experimental X-ray data showing both these phenomena are quantitatively compatible with the Mossbauer results.

Optical results of β-polymorph metal phthalocyanines can be interpreted in terms of the molecular orbital model, but analysis is complicated by intermolecular Davydov coupling.[48]

Conclusions—Bonding in Metal Tetrapyrroles

Our UHFS calculations produce ground-state wave functions in good qualitative agreement with experiment on the β-polymorphs of CoPc, FePc, and MnPc. There is much covalence, in particular strong σ donation of up and down spin into the $3d_{x^2-y^2}$ orbital from the lone pairs on N(2) atoms and π back-donation from down-spin $3d_{xz,yz}$ (ONLY) into the porphine ring. This latter is easily rationalized as the availability of a low-energy π^* orbital with the down spin, thus causing massive differential covalence between up and down spins. This differential covalence increases from CoPc to MnPc. In CoPc, the covalence is moderate, and the almost ionic level involving $3d_{xy}$, $9b_{2g}$-, is more stable than that involving $3d_{xz,yz}$, $6e_g$-. For FePc, these two orbitals are almost equal in energy, while the even greater covalence in MnPc makes the $6e_g$- level more stable than $9b_{2g}$-. This ordering of levels gives ground states of ${}^2A_{1g}$ for CoPc, ${}^3E_{2g}$ (with some possibility of ${}^3B_{2g}$) for FePc, and ${}^4E_g$ for MnPc. These ground states, the simple result of the trends observed in the calculation, agree well with the results of the spin- and charge-density experiments. We should emphasize that the assignment of the crystal ground states is by comparison of the theoretical and experimental charge and spin populations. The Xα relative state energies, while apparently agreeing with the crystal experimental results, are for the free molecule, and in addition this theory should not be relied on at these energy differences.

The large and unusual covalence effects alter the predictions for magnetic susceptibility, ESR, and Mossbauer effects so much relative to those for the same free metal ion ground states that ligand field type calculations based on them that use a single Steven's orbital reduction factor (e.g. ref 44) are misleading. Our covalent descriptions agree qualitatively with the results. In an empirical approach, quantitative calculations using large, anisotropic Steven's orbital reduction factors may be useful in the investigation of spin–orbit effects.

The UHF description of the ground states is a simple single determinant state for MnPc and CoPc. In a RHF description, very large components of excited states with spin in the π system of Pc, derived from $3d_{xz,yz}$, must be mixed into the ground state to reproduce, for example, the experimental ESR or pnd results. This illustrates the supposition of Sontum et al. that UHF descriptions may be much more useful in paramagnetic systems.

Our ab initio calculations agree well with experimental qualitatively, but the details are sensitive to basis set composition. We can speculate that our not very extensive free molecule Xα calculation agrees with experiments on the β-crystals because of a happy coincidence in relative 3d and Pc energies (in the Wolfsberg–Helmholz sense[55]) rather than from some more fundamental reason. Use of a better theoretical *free molecule* wave function may well agree less well with *crystal* experimental results.

As reflected by the observed changes in ground state from CoPc to MnPc, we infer that the electronic structures of these molecules are very sensitive to minor changes in the relative Pc and metal energies. Besides the difficulties this causes in theoretical calculations, it also explains the extreme sensitivity of cobalt tetrapyrrole ESR spectra to axial ligation. This same sensitivity, although not apparent in ESR spectra, appears in iron and manganese tetrapyrroles and has been seen in their charge densities.[29] In addition, in the Fe systems, small perturbations in ligation or the departure of the Pc geometry from D_{4h} symmetry can cause drastic changes in charge and, more particularly, spin densities due to the closeness of the spin–orbit-coupled ${}^3B_{2g}$ and ${}^3E_g$ lowest lying states.

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