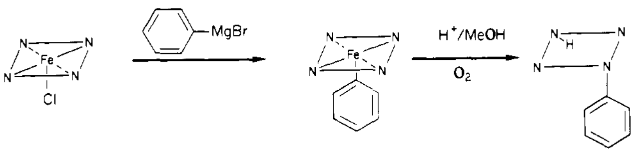
Scheme I



meso-phenyl protons on the same side of the porphyrin ring as the iron–phenyl will appear at higher field than the corresponding protons on the opposite side[8] are only consistent with the indicated assignments. The iron–phenyl proton signals, identified by their absence in the spectrum of the complex prepared with perdeuterated phenylmagnesium bromide, are at strikingly different positions. Whereas the meta protons are shifted to low field (13.22 ppm), the para and ortho protons (the latter exceptionally so) are shifted to high field (−25.52 and −80.67 ppm, respectively). The NMR spectrum indicates that the iron in PhFeTPP is in a low-spin rather than high-spin state because (a) the pyrrole protons appear at −20 ppm rather than +80 ppm and (b) the signal line widths[7] are in the 10–20-Hz rather than 100–300-Hz range.[9] A ferric low-spin state is consistent with that recently attributed to iron–alkyl porphyrin complexes.[10]

Solid PhFeTPP is stable at 25 °C in air but rapidly decomposes in solution in the absence of BHT to FeTPP (isolated and characterized as the chloride salt). The decomposition of PhFeTPP in an NMR tube is accompanied by the appearance of a sharp singlet at 7.25 ppm due (presumably) to benzene formation. No evidence was found in the NMR spectrum for the formation of phenol or biphenyl. If, however, PhFeTPP (0.13 mmol) in 50 mL of THF containing 0.025% BHT is treated overnight with 50 mL of 5% H_2SO_4 in methanol, *N*-PhTPP is obtained in 68% crystalline yield.[11] The high-field positions of the *N*-phenyl protons, noted previously with *N*-phenylprotoporphyrin IX,[2] clearly identify the product. The iron–nitrogen shift requires 1–2 h for completion and depends critically on the presence of oxygen. The yield of *N*-PhTPP is drastically reduced if oxygen is rigorously excluded. The shift is also highly sensitive to the solvent and acid used, although a detailed analysis of these parameters has not yet been completed. The iron–phenyl complex and the subsequent shift to nitrogen are also obtained with protoporphyrin IX, except that side products arise from reaction of the Grignard reagent with the esterified carbonyl side chains unless the Grignard reaction is run at low temperature.[13] The general reaction is given in Scheme I.

Iron–phenyl complexes with porphyrin and nonporphyrin ligands are known.[14] The shift of alkyl groups from cobalt to nitrogen[15] and a similar shift of a vinylidene carbene–iron complex have recently been reported.[16] The present example, however, is the first in which the migration of an aryl group is demonstrated. The stringent parallels in the behavior of the hemoglobin–phenylhydrazine intermediate and the present model system not only substantiate our postulate that the former is an iron–phenyl complex but also provide the clearest demonstration that iron–carbon complexes are formed with hemoproteins.[17]

Registry No. Fe(TPP)Cl, 16456-81-8; PhFeTPP, 70936-44-6; *N*-PhTPP, 81856-91-9; phenyl bromide, 108-86-1.

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(8) The peripheral protons on the same side of the porphyrin as the iron–phenyl group are shifted up field by the phenyl group ring current.

(9) La Mar, G. N.; Walker (Jensen), F. A. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 4, pp 61–157.

(10) Lexa, D.; Mispelter, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 6806–6812.

(11) The product was isolated by partitioning the reaction mixture between 100 mL of CH_2Cl_2 and 200 mL of H_2O, separating and washing the organic layer with aqueous $NaHCO_3$, drying (Na_2SO_4), solvent removal, and chromatography on basic alumina (CH_2Cl_2). The bright green porphyrin was crystallized from benzene–petroleum ether (bp 60–110 °C fraction); λ_{max} (ϵ_M) ($CHCl_3$) 444 (385 000), 550 (sh) (17 200), 595 (36 700), 633 (sh) (14 000), 705 nm (8800); λ_{max} of the dication ($CHCl_3$, 2% trifluoroacetic acid) 457 (512 000), 694 nm (87 900); ^1H NMR (80 MHz, $CDCl_3$) δ 8.68 (s, 2 H, 5,6-pyrrole H), 8.1–8.4 (m, 16 H, 3,4,7,8-pyrrole H, *meso*-Ph *o*-H), 7.7 (m, 12 H, *meso*-Ph *m*- and *p*-H), 7.4 (s, 2 H, 1,2-pyrrole H), 5.6 (t, 1 H, N–Ph *p*-H), 5.24 (t, 2 H, N–Ph *m*-H), 3.00 (d, 2 H, N–Ph *o*-H); mass spectrometric molecular ion (electron impact, 70 eV) *m*/*e* 690. The *N*-phenyl proton assignments are based on decoupling experiments, but the porphyrin ring protons have been assigned by analogy to assignments made for *N*-CH_3TPP.[12]

(12) Al-Hazimi, H. M. G.; Jackson, A. H.; Johnson, A. W.; Winter, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 98–103.

(13) The dimethyl ester of *N*-phenylprotoporphyrin IX obtained from the rearrangement reaction is identical with the product previously obtained in the reaction of heme with phenylhydrazine.[2] The phenyl–iron complex, in addition to NMR signals attributable to the protoporphyrin IX framework, exhibits signals for the iron–phenyl group at 13.94 (meta protons), −21.64 (para proton), and −77.45 ppm (ortho protons). The positions of these peaks are similar to those of the analogous protons in the TPP system (Figure 1).

(14) (a) Floriani, C.; Calderazzo, F. *J. Chem. Soc. A* **1971**, 3665–3669. (b) Rakowski, M. C.; Busch, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 2570–2571. (c) Goedken, V. L.; Peng, S. M.; Park, Y. *J. Am. Chem. Soc.* **1974**, *96*, 284–285. (d) Clarke, D. A.; Dolphin, D.; Grigg, R.; Johnson, A. W.; Pincock, H. A. *J. Chem. Soc. C* **1968**, 881–885.

(15) (a) Dolphin, D.; Halko, D. J.; Johnson, E. *Inorg. Chem.* **1981**, *20*, 4348–4351. (b) Callot, H. J.; Schaeffer, E. *Tetrahedron Lett.* **1980**, 1335–1338.

(16) (a) Lange, M.; Mansuy, D. *Tetrahedron Lett.* **1981**, 2561–2564. (b) Wisnieff, T. J.; Gold, A.; Evans, S. A. *J. Am. Chem. Soc.* **1981**, *103*, 5616–5618.

(17) Support of this research by NIH Grants AM-30297 and GM-25515 and by the Alfred P. Sloan Foundation is gratefully acknowledged. O.A. is on leave from the Universidade de Sao Paulo.

Agreement between Transition-Metal Orbital Populations from X-ray and Polarized Neutron-Scattering Experiments

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We have recently developed formalisms relating transition-metal d-orbital occupancies to the population of multipolar density functions that can be obtained by least-squares refinement of accurate X-ray diffraction data.[1,2] The formalisms have been applied in a number of studies, among which the analysis of the electronic structure of the mineral pyrite (FeS_2)[3] and the transition-metal complex cobalt tetraphenylporphyrin (CoTPP).[4] They generally provide orbital populations that are in agreement with the ordering of the electronic energy levels according to theoretical considerations. Thus, in FeS_2 (local symmetry at the Fe site $\bar{3}m$) the a_g (t_{2g}) orbital which is ligand-field stabilized is fully occupied by 1.98 (12) electrons, while a partial occupancy of 0.66 (15) electrons is obtained for the destabilized e_g' orbital. This partial occupancy of a destabilized orbital in a low-spin complex suggests a covalent metal–ligand interaction commonly described by σ donation. Thus, the results offer the possibility for a quantitative assessment of the importance of covalent interactions.

Further evidence for this interpretation has become available from polarized neutron diffraction measurements that can be interpreted in terms of the *spin* populations of the atomic orbitals by the application of relations between the spin density and spin

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(1) Stevens, E. D.; Coppens, P. *Acta Crystallogr., Sect A* **1979**, *A35*, 536–539.

(2) Stewart, R. F. *Acta Crystallogr., Sect A* **1976**, *A32*, 565–574. Hansen, N. F.; Coppens, P. *Ibid.* **1978**, *A34*, 909–921.

(3) Stevens, E. D.; DeLucia, M. L.; Coppens, P. *Inorg. Chem.* **1980**, *19*, 813–820.

(4) Stevens, E. D. *J. Am. Chem. Soc.* **1981**, *103*, 5087–5095.

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Table I. Experimental and Theoretical Orbital Populations[a]

	X-ray charge	neutron spin →	charge			theoretical charge[7]	
	CoTPP[4,8]	βCoPc[6]	βCoPc[6,9]	ρ_α[b]	ρ_β[b]	βCoPc	CoTPP
$b_1(d_{x^2-y^2})$	0.83 (20)	−0.21 (10)	0.21	0.3	0.5	0.24	0.26
$a_1(d_{z^2})$	0.92 (20)	0.79 (12)	1.21	0.8_6	0.0_6	1.02	1.06
$b_2(d_{xy})$	1.64 (20)	0.40 (10)	1.60	1.0	0.6	1.78	1.76
$e(d_{xz}, d_{yz})$	3.62 (20)	0.34 (20)	3.66	2.0	1.6	3.96	3.93
4s		−0.14 (16)	0.14 or 1.86		0.14		

[a] Numbers in brackets represent standard deviations derived from the least squares fit to the X-ray and neutron data. [b] $\rho_\alpha = \{\rho_{\text{charge}}(\text{X-ray}) + \rho_{\text{spin}}(\text{neutron})\}/2$; $\rho_\beta = \{\rho_{\text{charge}}(\text{X-ray}) - \rho_{\text{spin}}(\text{neutron})\}/2$.

orbital populations, which are analogous to those applied to the X-ray results.[5]

A comparison may be made between CoTPP and β-cobalt phthalocyanine, (CoPc), the spin density of which has recently been analyzed by Williams, Figgis, and Mason.[6] In both compounds the cobalt atom is surrounded by a square-planar array of pyrrole-ring nitrogen atoms, so that the first coordination spheres are very similar. The similarity of the cobalt electron configuration in CoTPP and the β modification of CoPc is supported by theoretical calculations.[7]

The experimental populations, summarized in Table I, can be interpreted in two different ways. Cobalt atomic orbital charges derived from the spin populations by using electroneutrality considerations[9] are listed in the fourth column of the table and compare remarkably well with the charges from the X-ray experiment on CoTPP listed in the second column except for the orbital $d_{x^2-y^2}$. The neutron experiment is not sensitive to the population of this metal–ligand bonding orbital in which electron spins are mostly paired.[5] A second approach is represented by the entries in columns five and six. Since the spin density is given by $\rho_{\text{spin}} = \rho(\uparrow) - \rho(\downarrow)$ and the charge density by $\rho_{\text{charge}} = \rho(\uparrow) + \rho(\downarrow)$ the results may be compared to give the $\alpha(\uparrow)$ and $\beta(\downarrow)$ spin populations. The close to integral values obtained for the α population of the d_{xz}, d_{yz}(e), $d_{xy}(b_2)$ and $d_{z^2}(a_1)$ orbitals are in agreement with the maximum mulitplicity (Hund) rule. In the $d_{x^2-y^2}(b_1)$ orbital, spins are almost completely paired as expected. As in pyrite its occupancy is a measure of the covalency of the metal–ligand interaction. The metal-bonding σ orbital may be written as[10]

$$\psi_{x^2-y^2} = N_\sigma[d_{x^2-y^2} - \tfrac{1}{2}\lambda_\sigma(p_{x1} - p_{x3} + p_{y2} - p_{y4}) - \tfrac{1}{2}\lambda_s(s_1 + s_3 - s_2 - s_4)]$$

where the p_{xi} are the appropriately oriented ligand p orbitals on the *i*th nitrogen atom and the s are the corresponding s orbitals. In a first approximation, neglecting cobalt–nitrogen overlap, which is quite small,[11] the spin-paired population in the $d_{x^2-y^2}$ orbital is then given by $P(d_{x^2-y^2}) = 2N_\sigma^2 = 2(1 + \lambda_\sigma^2 + \lambda_s^2)^{-1}$, assuming double occupancy of the bonding orbital $\psi_{x^2-y^2}$. Substitution of the experimental value for the paired population of 0.6 electrons gives $\lambda_\sigma^2 + \lambda_s^2 = 2.3$,[12] indicating a dominant ligand contribution to the bonding orbital.

Finally, we note that the experimental orbital occupancies are in qualitative agreement with a minimal basis set calculation with configuration interaction reported by Lin[7] (columns seven and eight of the table). The agreement between the two sets of experimental results provides support for both techniques and indicates the potential of accurate diffraction methods in the elucidation of the detailed electronic structure of transition-metal complexes.

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Registry No. CoTPP, 14172-90-8; β-CoPc, 3317-67-7.

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(7) Lin, W. C. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 355–377.

(8) The numbers in this column differ slightly from those of ref 4 due to correction of an error in the earlier results.

(9) The charge populations are obtained by regarding the positive spin occupancies as holes in a filled d^{10} shell (ref 6).

(10) Tofield, B. C. *Struct. Bonding (Berlin)* **1975**, *21*, 1.

(11) Kashiwagi, H.; Takada, T.; Obara, S.; Miyoshi, E.; Ohno, K., *Int. J. Quant. Chem.* **1978**, *14*, 13–27.

(12) This number is reduced to about 2.2 if values of 0.05 are used for the metal–ligand d-σ and d-s overlap integrals.