Inorg. Chem. **1996,** *35,* 7935−7937

Evidence for Porphyrin (π)−Chlorine (p) Orbital Overlap in the π-Cation Radicals of Zinc(II) and Magnesium(II) Tetrakis(*o*-dichlorophenyl)porphyrin

William A. Kalsbeck, Jyoti Seth, and David F. Bocian*

Department of Chemistry, University of California,
Riverside, California 92521-0403

Received July 17, 1996

Introduction

Metalloporphyrins containing electron-withdrawing peripheral substituents are of interest owing to their potential utility as catalysts in hydrocarbon oxidation reactions.[1] Electron-withdrawing substituents raise the redox potential of the porphyrin macrocycle,[2] thus stabilizing it with respect to oxidative damage. Depending on the placement of the electron-withdrawing groups, the relative energies of the two highest occupied molecular orbitals (HOMOs) of metalloporphyrins (a_{1u} and a_{2u}) can also be altered.[3−7] In extreme cases, the addition of substituents can reverse the ordering of the a_{1u} and a_{2u} orbitals relative to that found in the unsubstituted parent complex. For example, the HOMO of metallotetraphenylporphyins (M(TPP)) (and most other metallotetraarylporphyrins) is the a_{2u} orbital.[3,4,8,9] However, perfluorination of the *meso*-phenyl groups results in complexes in which the HOMO is the a_{1u} orbital.[5,6c] The orbital reversal occurs because the a_{2u} orbital undergoes a significant energetic stabilization owing to its large electron density on the *meso*-carbon atoms.[8] Electron density is absent on the *meso*-carbon atoms for the a_{1u} orbital because these atoms fall on nodal planes.

For tetraarylporphyrins in which the electron-withdrawing capacity of the aryl groups is less than that of the perfluoro species, the energetic ordering or the a_{1u} and a_{2u} orbitals is more difficult to assess. Tetrakis(*o*-dichlorophenyl)porphyrin (DCPP) is a particularly interesting representative of this latter group. Density functional calculations on free base DCPP predict an a_{2u} HOMO.[4] Nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and resonance Raman (RR) studies on the π-cation radical of the oxoiron(IV) complex of DCPP ($(OFe^{IV}(DCPP^{\bullet})^+)$) support an a_{2u} HOMO for this species.[6a,c,7] However, certain features in the RR spectrum led to the suggestion that the electronic ground state of OFe^{IV}-$(DCPP^{\bullet})^+$ is better characterized as a $^2A_{2u}/^2A_{1u}$ quantum admixture.[7b] In the case of a strong quantum admixture, it is inappropriate to use the molecular orbitals a_{1u} and a_{2u} as descriptors of the ground state or to assign a particular orbital as the HOMO. On the other hand, EPR and RR data obtained for $Zn^{II}(DCPP^{\bullet})^+$ were interpreted as indicative of a pure $^2A_{1u}$ ground state and hence an a_{1u} HOMO.[5] A $^2A_{1u}$ ground state for $Zn^{II}(DCPP^{\bullet})^+$ is difficult to rationalize given the relatively modest electron-withdrawing capabilities of *o*-dichloro vs perfluoro substituents.[4] The EPR signal for $Zn^{II}(DCPP^{\bullet})^+$ was also reported to exhibit a g value of ~2.012.[5a] This value is significantly different from that of other metalloporphyrin π-cation radicals which contain closed shell metal ions.[2,9] All of these latter complexes exhibit g values near the free electron value $g_e = 2.0023$.

The uncertain nature of the electronic ground state of metallo-$(DCPP^{\bullet})^+$ complexes and in particular, the unusual g value reported for $Zn^{II}(DCPP^{\bullet})^+$ prompted us to carefully examine the EPR spectral features of $Zn^{II}(DCPP^{\bullet})^+$ and $Mg^{II}(DCPP^{\bullet})^+$. RR data were also acquired for the latter complex. EPR and RR data have not been previously reported for $Mg^{II}(DCPP^{\bullet})^+$. This complex is of particular interest because it can be formed with either one or two axial ligands. The studies reported in this note provide a better picture of the electronic ground state of metallo$(DCPP^{\bullet})^+$ complexes. More interestingly, they provide clear evidence for overlap between the a_{2u} orbital of the porphyrin ring and p orbital(s) of the *o*-dichloro substituents.

Experimental Section

$H_2(DCPP)$ was obtained from Midcentury and used as received. Zn(II) and Mg(II) were inserted via the DMF method.[10] The Mg(II) complex was obtained from the chloride salt (Aldrich) and the Zn(II) complex was obtained from the acetate salt (Aldrich). The complexes were purified on basic alumina columns, using CH_2Cl_2 as the eluting solvent. The electrochemical and spectroscopic studies were performed on samples prepared in CH_2Cl_2 or an acetonitrile:THF (~90%:10%) mixture. The mixture yields bis-axially-ligated $Mg^{II}(DCPP)$ as evidenced by the red shift of the optical spectrum relative to neat CH_2Cl_2 or acetonitrile.[11] CH_2Cl_2 (Aldrich, HPLC Grade), was purified by vacuum distillation from P_2O_5 followed by another distillation from CaH_2. Acetonitrile (Burdick and Jackson) was used as received. THF (Aldrich, HPLC Grade) was stirred over sodium metal and distilled under vacuum. The supporting electrolyte used for the oxidations was ~0.1 M tetrabutylammonium hexafluorophosphate (Aldrich; recrystallized three times from methanol and dried at 110 °C *in vacuo*).

The electrochemical oxidations were conducted in a standard three-compartment cell by using standard electrochemical instrumentation.[12] The electrochemical cell was housed in a nitrogen-filled Vacuum Atmospheres glovebox (Model HE-93) equipped with a Dri-Train (Model 493). The integrity of the cations was confirmed by cyclic voltammetry and absorption spectroscopy. Subsequent to oxidation, the samples were transferred to a optical cuvette (absorption) or a quartz tube (EPR). RR spectra were obtained from samples in the sealed electrochemical cell maintained under electrochemical potential. The RR spectra of the neutral complexes were obtained from samples in sealed capillary tubes.

The EPR spectra were recorded on a Bruker ER 200D X-band spectrometer. Temperature control was achieved by using a Bruker

---

(1) For selected recent review on metalloporphyrin-catalyzed oxygenation reactions see: (a) Bruice, T. C.; *Acc. Chem. Res.* **1991**, *24*, 243. (b) Bruice, T. C.; *Acc. Chem. Res.* **1992**, *25*, 314. (c) Stern, M. K.; Groves, J. T. In *Manganese Redox Enzymes*; Pecoraro, V. L., Ed.; VCH: New York, 1992; Chapter 11. (d) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411. (e) Mansuy, D.; Battioni, P. In *Bioinorganic Catalysis*; Reedjik, J.; Ed.; Marcel Dekker: New York, 1993; pp 395−424. (f) Mansuy, D. *Coord. Chem. Rev.* **1993**, *125*, 129. (g) *Metalloporphyrins in Catalytic Oxidation*; Sheldon, R. A., Ed.; Marcel Dekker: New York, 1994. (h) *Metalloporphyrin Catalyzed Oxidations*; Montanari, F., Casella, L., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1994.

(2) Felton, R. H. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. V, pp 53−126.

(3) Skillman, A. G.; Collins, J. R.; Loew, G. H. *J. Am. Chem. Soc.* **1992**, *114*, 9538.

(4) Ghosh, A. *J. Am. Chem. Soc.* **1995**, *117*, 4691.

(5) (a) Gross, Z.; Barzilay, C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1615. (b) Barzilay, C; Sibilia, S. A.; Spiro, T. G.; Gross, Z. *Chem.*−*Eur. J.* **1995**, *1*, 222.

(6) (a) Fujii, H. *J. Am. Chem. Soc.* **1993**, *115*, 4641. (b) Fujii, H. *Chem. Lett.* **1994**, 1491. (c) Fujii, H. *Inorg. Chem.* **1996**, *35*, 2373.

(7) (a) Mandon, D.; Weiss, R.; Jayaraj, K.; Gold, A.; Terner, J.; Bill, E.; Trautwein, A. X. *Inorg. Chem.* **1992**, *31*, 4404. (b) Jayaraj, K.; Terner, J.; Gold, A.; Roberts, D. A.; Austin, R. N.; Mandon, D.; Weiss, R.; Bill, E.; Müther, M.; Trautwein, A. X. *Inorg. Chem.* **1996**, *35*, 1632.

(8) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. III, pp 1−165.

(9) Fajer, J.; Davis, M. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. IV, pp 197−256.

(10) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, *J. Inorg. Nucl. Chem.* **1979**, *32*, 2443.

(11) Buchler, J. W. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 203−232.

(12) Diers, J. R.; Bocian, D. F. *J. Phys. Chem.* **1994**, *98*, 12884.

S0020-1669(96)00835-X CCC: $12.00

Table 1. EPR Parameters of $M^{II}(DCPP^{\bullet})^{+}$

species	g_{av}[a]	$g_{\perp}$[b]	$g_{\parallel}$[b]	$a_{\perp}$ (G)[b]	$a_{\parallel}$ (G)[b]	$\Delta_{\perp}$ (G)[b]	$\Delta_{\parallel}$ (G)[b]
				295 K			
Zn	1.999	2.001	1.995	1.18	1.43	2.86	7.16
Mg-**5c**	1.998	2.000	1.994	1.43	1.43	3.79	5.57
Mg-**6c**	1.999	1.999		0.0		3.86	
				100 K			
Zn[c]	1.999	2.003	1.991	0.54	0.72	1.53	1.26
	1.997	1.989	2.014	1.44	0	8.26	1.42
Mg-**5c**	1.999	(2.004, 1.999)[d]	1.995	(0.41, 1.14)[d]	1.43	(1.43, 4.29)[d]	7.16
Mg-**6c**	1.999	2.003	1.990	0.27	0.27	1.51	9.34

[a] For the 295 K spectra, g_{av} was measured at the zero crossing point. For the 100 K spectra, g_{av} was calculated from values obtained from simulations of the spectra. [b] Values obtained from simulations of the spectra using a Lorentzian line shape, except for Mg-**6c**, for which a Gaussian line shape was required. The parameter, Δ, corresponds to the fwhm. [c] Simulation of the 100 K spectrum requires inclusion of at least two signals (see text). [d] Simulations indicate that this signal is slightly rhombic.

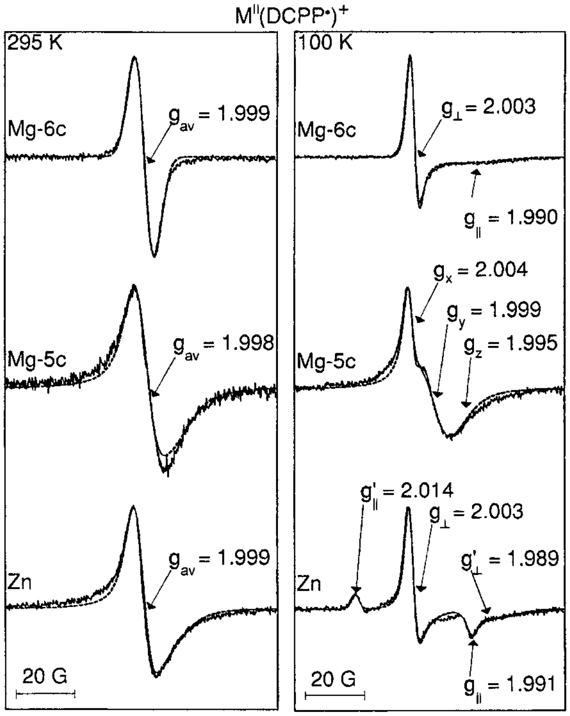

Figure 1. Ambient (left panel) and low (right panel) temperature X-band EPR spectra of the $M^{II}(DCPP^{\bullet})^{+}$ complexes. The dashed lines are spectra simulated using the parameters given in Table 1.

continuous flow N_2 cryostat. The *g* values were measured with a Bruker ER 035M NMR gaussmeter and a Hewlett-Packard 3550B microwave frequency counter. The RR spectra were acquired with a triple spectrograph (Spex 1877) using collection optics and a detection system which have been previously described.[13] The excitation wavelengths were provided by the outputs of a Kr ion laser (Coherent Innova 200-K3). The laser powers were typically 2−5 mW.

Results and Discussion

The ambient-temperature (295 K) EPR spectra of electrochemically generated $Zn^{II}(DCPP^{\bullet})^{+}$ and mono- and bis-axially-ligated $Mg^{II}(DCPP^{\bullet})^{+}$ (designated Mg-**5c** and Mg-**6c**, respectively) are shown in Figure 1 (left panel). At ambient temperature, the signals from all three complexes are relatively narrow and exhibit no resolved hyperfine structure. The absence of visible hyperfine structure was previously invoked as evidence for an $^{2}A_{1u}$ ground state for $Zn^{II}(DCPP^{\bullet})^{+}$.[5] All three $M^{II}(DCPP^{\bullet})^{+}$ complexes also exhibit g_{av} ~2.00, slightly lower than g_e. The signal for Mg-**6c** is narrower than those of $Zn^{II}(DCPP^{\bullet})^{+}$ and Mg-**5c** and quite symmetric. The signals for the latter two complexes are slightly asymmetric. The general appearance (shape and width) of the EPR signal obtained for electrochemically generated Mg-**6c** is qualitatively the most similar to that previously reported for chemically generated $Zn^{II}(DCPP^{\bullet})^{+}$.[5] As was previously noted, however, this latter complex was reported to have a *g* value of ~2.01. Simulations of the EPR spectra confirm that the signal for Mg-**6c** is isotropic whereas those of $Zn^{II}(DCPP^{\bullet})^{+}$ and Mg-**5c** are slightly anisotropic and characteristic of an approximately axially symmetric spin system. The simulations also indicate that the EPR signals for all three complexes can be adequately simulated without including ^{14}N hyperfine coupling. However, in the case of $Zn^{II}(DCPP^{\bullet})^{+}$ and Mg-**5c**, the detailed shapes of the EPR signals are fit far more satisfactorily if ^{14}N hyperfine couplings are included. Indeed, the best fits are obtained with hyperfine couplings in the 1.0−1.4 G range. These values approach those of $Zn^{II}(TPP^{\bullet})^{+}$ and $Mg^{II}(TPP^{\bullet})^{+}$ for which the ^{14}N hyperfine couplings are ~1.4 G.[9] The parameters used in the simulations of the EPR spectra are summarized in Table 1.

The low-temperature (100 K) EPR spectra of electrochemically generated $Zn^{II}(DCPP^{\bullet})^{+}$, Mg-**5c** and Mg-**6c** are shown in Figure 1 (right panel). The *g* values indicated were obtained from simulations of the EPR spectra. The parameters used in the simulations are summarized in Table 1. Temperature-dependent EPR studies (not shown) indicate that the signals for all three $M^{II}(DCPP^{\bullet})^{+}$ complexes narrow as the temperature is lowered, and no hyperfine splittings are resolved. Upon freezing of the solvent, no changes are observed in the signals as the temperature is lowered further. The EPR features of Mg-**6c** are the least complicated. The signal for this complex is distinctly anisotropic and characteristic of an axially symmetric spin system with a narrow $g_{\perp} = 2.003$ feature and a very broad $g_{\parallel} = 1.990$ feature. The $g_{\parallel}$ signal is sufficiently broad that it could be easily overlooked. The EPR signal for Mg-**5c** is also anisotropic and exhibits both narrow and broad features. The signal for this latter complex is slightly rhombic ($g_x = 2.004$, $g_y = 1.999$, $g_z = 1.995$) rather than axial. In the case of $Zn^{II}(DCPP^{\bullet})^{+}$, it was not possible to obtain a reasonable fit to the spectrum assuming a single species is present. The spectrum can be fit using the superposition of signals from two species; however, these fits are not unique. One reasonable fit is shown in the figure and is obtained from a superposition of two different axial signals one with $g_{\parallel} = 1.991$ and $g_{\perp} = 2.003$ (60%) and the other with $g'_{\parallel} = 2.014$ and $g'_{\perp} = 1.989$ (40%). Combinations of axial and rhombic signals can also adequately account for the spectrum (not shown). Another noteworthy feature of the EPR spectra is that the average of the *g* values of the anisotropic signals observed at low temperature is essentially

---

(13) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578.

identical to the g_{av} value observed at ambient temperature. This observation suggests that the characteristics of the electronic ground state are approximately the same at ambient and low temperatures.

The ambient-temperature, Soret-excitation RR spectrum of Mg-**5c** was obtained (not shown) for comparison that was previously reported for $Zn(DCPP^{\bullet})^{+}$.[5b] A reliable spectrum of Mg-**6c** could not be obtained owing to severe photolysis problems. In the parent neutral of Mg-**5c**, the ν_2 porphyrin mode is observed near 1549 cm^{-1} compared with 1550 cm^{-1} for Zn(DCPP). Formation of Mg-**5c**, upshifts ν_2 and a doublet structure is observed at 1555 and 1573 cm^{-1}. This behavior and the frequencies of the doublet are essentially identical to those observed upon formation of $Zn(DCPP^{\bullet})^{+}$.[5b] The doublet structure has been previously rationalized in terms of a Fermi resonance between ν_2 and a phenyl ring mode.[5b] The upshift of ν_2 was taken as further evidence for a $^2A_{1u}$ ground state.

The significant anisotropy observed in the EPR signals of the three $M^{II}(DCPP^{\bullet})^{+}$ complexes studied herein indicates that the properties of the electronic ground state are more complicated than previously thought. One possible origin for the g anisotropy observed for $Zn^{II}(DCPP^{\bullet})^{+}$ is that metal-orbital character is mixing into the porphyrin π-orbitals.[9] This type of mixing has been shown to be responsible for the anisotropic EPR spectra observed for the π-anion radicals of Zn(II) porphyrins.[14] However, this mechanism cannot plausibly account for the anisotropy observed for $Mg^{II}(DCPP^{\bullet})^{+}$. Accordingly, it seems more reasonable that the anisotropy observed for both the Mg(II) and Zn(II) complexes has a common origin. The only remaining atoms in the complexes with appreciable spin−orbit coupling are the chlorine atoms ($\lambda = 586$ cm^{-1}).[15] The porphyrin−chlorine interaction could be either indirect, involving the intervening bonds of the phenyl ring, or direct, involving overlap of the porphyrin and chlorine orbitals. Regardless, the interaction must involve the p orbitals of the chlorine atoms in order to introduce angular momentum into the ground state wave function for the π-cation radical.

The effects axial ligands have on the EPR spectral features of $Mg^{II}(DCPP^{\bullet})^{+}$ along with the general structural characteristics of tetraarylporphyrins argue that the chlorine−porphyrin interaction is direct, involving overlap of the p orbitals on the chlorine atoms and the *meso*-carbon atoms of the porphyrin ring. The rationale for this assessment is as follows: The torsional angles between phenyl and the porphyrin rings of both neutral M(TPP) and $M(TPP^{\bullet})^{+}$ are relatively large, 40−60°.[16] In M(DCPP) complexes, the bulky *o*-dichloro substituents further restrict the rotation of the aryl rings, thus favoring large torsional angles.[17] Othogonality or significant noncoplanarity between the porphyrin and phenyl rings minimizes through-bond interaction between the p orbitals of the *meso*-carbon and chlorine atoms. On the other hand, large torsional angles facilitate direct porphyrin−chlorine interactions. These interactions would maximize when the porphyrin and phenyl rings are orthogonal. In this orientation, the center-to-center distance between the chlorine and *meso*-carbon atoms is ∼3 Å.[18] This distance places these atoms well within van der Waals contact.[19b] The presence of axial ligands could additionally influence the orientation of the sterically constrained *o*-dichlorophenyl groups. When two axial ligands are present, the additional steric interactions could lock in the conformation of the aryl groups in a nearly orthogonal orientation. This would lead to a relatively symmetrical structure which would in turn give rise to an axially symmetric EPR signal such as that observed for Mg-**6c**. On the other hand, if only a single (or no) axial ligands are present, the *o*-dichlorophenyl groups would be free to explore a larger (but still limited) range of conformational space. This would lead to a relatively asymmetric structure and possibly multiple conformers. This could explain why rhombic and multiple EPR signals are observed for Mg-**5c** and $Zn^{II}(DCPP^{\bullet})^{+}$, respectively.

Regardless of the origin of the porphyrin−chlorine interactions, these interactions can only occur through the a_{2u} molecular orbital of the porphyrin ring. This in turn implies that the electronic ground states of all three $M^{II}(DCPP^{\bullet})^{+}$ complexes contain substantial, if not dominant, $^2A_{2u}$ character. These results indicate that neither the absence of ^{14}N hyperfine splittings nor upshifts in the ν_2 porphyrin mode can be taken as unequivocal evidence for an $^2A_{1u}$ ground electronic state. Most likely, the ground states of $Zn^{II}(DCPP^{\bullet})^{+}$ and $Mg^{II}(DCPP^{\bullet})^{+}$ are $^2A_{2u}/^2A_{1u}$ quantum admixtures as has been previously suggested for $OFe^{IV}(DCPP^{\bullet})^{+}$.[7b] The apparent absence of ^{14}N hyperfine splittings (most apparent for Mg-**6c**) could be due to reduced ^{14}N coupling resulting from the admixture. On the other hand, the overlap between the porphyrin a_{2u} and chlorine p orbitals may play a more direct role in reducing the ^{14}N hyperfine coupling. In particular, this overlap could redirect spin density away from the pyrrole nitrogen towards the *meso*-carbons atoms (and to some extent onto the chlorine atoms). The spin density on the pyrrole nitrogen atoms in a pure $^2A_{2u}$ π-cation radical is relatively small (∼0.05/^{14}N-atom). Redirection of 0.02−0.03/^{14}N-atom would render the hyperfine splittings unobservable. Indeed, this effect could conceivably render the ^{14}N hyperfine splittings unobservable for a π-cation which has a pure $^2A_{2u}$ ground state.

Acknowledgment. This work was supported by Grant GM 36243 (D.F.B.) from the National Institute of General Medical Sciences. We thank Dr. J. Fajer for helpful discussions.

IC9608354

---

(14) Seth, J.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 143.

(15) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Chapman and Hall: London, 1979; p 138.

(16) (a) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding* **1987**, *64*, 1. (b) Scheidt, W. R.; Mondal, J. U.; Eigenbrot, C. W.; Adler, A.; Radonovich, L. J.; Hoard, J. L. *Inorg. Chem.* **1986**, *25*, 795. (c) Spaulding, L. D.; Eller, P. G.; Bertnard, J. A.; Felton, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 982. (d) Barkigia, K. M.; Spaulding, L. D.; Fajer, J. *Inorg. Chem.* **1983**, *22*, 34.

(17) Crossley, M. J.; Field, L. D.; Forster, A. J.; Harding, J. M.; Sternhell, S. *J. Am. Chem. Soc.* **1987**, *109*, 341.

(18) This distance was calculated using bond lengths and angles determined for M(TPP) complexes[16] and a C−Cl bond length of 1.77 Å.[19a]

(19) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper & Row: New York, 1978: (a) Table 1; (b) Table F.1.