Notes

π-Cation Radicals of Copper(II) Derivatives of Short Chain Basket Handle Porphyrins

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Introduction

A number of metallotetraphenylporphyrin (MTPP) π-cation radicals which have been structurally characterized are found to be dimeric with ruffled cores in the solid state.[1,2] Reed and coworkers suggested that the ruffled core in π-cation radicals is a necessary molecular distortion required to allow dimerization. To prove this, the structure of CuTMP$^{\bullet+}$ (copper(II) tetramesitylporphyrin[3] radical cation), which cannot form a dimer due to the bulky *o*-methyl substituent, was solved and the structure indicates the presence of flat core. In the present paper we wish to report studies on π-cation radicals of a few deformed short-chain basket-handle copper porphyrins (Figure 1). These porphyrin radical cations are interesting from the following structural point of view: (a) the short bridging chain across the porphyrin periphery prevents the dimerization observed for many MTPP$^{\bullet+}$ radicals, and (b) the porphyrin core is highly deformed in neutral derivatives in solid and solution phase[4–8] and the deformed core is retained upon radical formation. It has been shown that the π-cation radicals are diamagnetic both in solid and in CD_2Cl_2 solution unlike CuTPP$^{\bullet+}$ [2,9] due to antiferromagnetic coupling facilitated by ruffling of the porphyrin core. In addition to the spectroscopic evidence, molecular mechanics simulations using MOBY[10] have been done to establish the presence of ruffling in the porphyrin core.

Experimental Section

Materials. Porphyrins were synthesized and characterized as reported previously.[4,8] The oxidant tris(*p*-bromophenyl)ammonium hexachloroantimonate was procured from E. Merck. CH_2Cl_2 was dried twice over anhydrous $CaCl_2$ and distilled over P_2O_5.

Synthesis of [Cu((PSI)Br$_8$)][SbCl$_6$]. Cu((PSI)Br$_8$) (0.010 g, 0.006 mmol) in CH_2Cl_2 (10 cm^3) was stirred for 10 min under an argon atmosphere and 1.1 equiv of tris(p-bromophenyl)ammonium hexachloroantimonate (0.006 g, 0.069 mmol) was added slowly to it. A deep green color developed immediately, and stirring was continued for 4 h. The progress of the reaction was monitored with a UV–vis spectrophotometer. After filtration, the solvent was evaporated in vacuo, and the green powder obtained was dissolved in a minimum amount of CH_2Cl_2 and precipitated with hexane. The product was filtered and washed several times with a dichloromethane–hexane (1:9) solvent mixture, dried and stored in vacuo (yield 0.010 g, 80%). Anal. Calcd for $C_{60}H_{32}CuCl_6Br_8N_4Sb$: C, 37.69; H, 1.69; N, 2.92. Found: C, 37.02; H, 1.85; N, 2.75. UV–vis λ_{max} (nm) (CH_2Cl_2): 687, 618 (sh), and 412. A similar procedure was used for the synthesis of other derivatives. UV–vis λ_{max} (nm) (CH_2Cl_2): for [CuHexylI][SbCl$_6$], 684, 614 (sh), 410; for [Cu(PSI)][SbCl$_6$], 686, 610 (sh), 414; for [Cu((MSI)Cl$_8$)][SbCl$_6$], 701, 414.

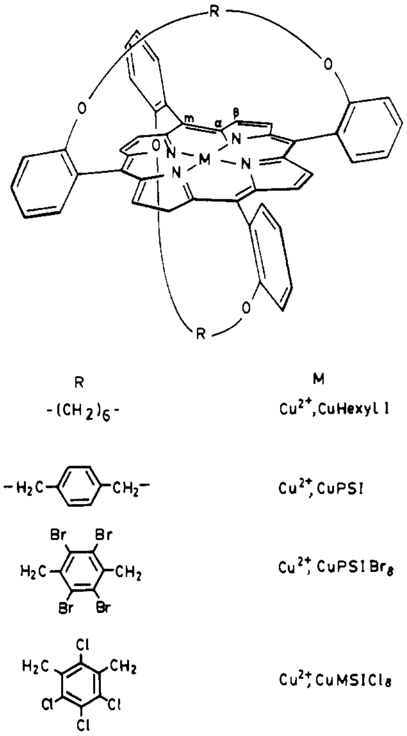

Figure 1. Structures of copper derivatives of short-chain basket-handle porphyrins.

Instrumentation. The details of UV–vis, IR, CV, NMR, and ESR spectrometers employed in the present study are described in our earlier work.[4,8] Variable-temperature magnetic susceptibilities on powder were measured between 80 and 300 K on a computer-controlled Faraday magnetometer, Models 300 and 321, George Associates, Berkeley, CA. A data translation A/D board and AT computer were used to monitor the microbalance output and temperature readings. The instrument was calibrated with a Hg[Co(NCS)$_4$] and has an absolute accuracy of 0.5%. The raw data were corrected for the susceptibility of the holder and diamagnetism of the ligands.

For resonance Raman measurements, the samples in CH_2Cl_2 were taken in optical quality liquid cells, and 457.9-nm radiation from a Spectra-Physics Model 2030-15 argon ion laser was used as an excitation source. A Spex triple mate in conjunction with a micro assembly and liquid-N_2-cooled CCD detector assisted by DM-3000 computer interfacing were used to record the spectra. Only 8 mW of the laser power was used at the sample to avoid any optical damage at the focused spot. The scattered light were collected in the 180° backscattering geometry. Instrumental slit width, resolution, and wavenumber accuracy are around 2, 1.5, and ±2 cm^{-1}, respectively.

Results

Treatment of copper derivatives of various deformed porphyrins with tris(p-bromophenyl)ammonium hexachloroantimonate in

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(1) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding* **1987**, *64*, 1.

(2) Erler, B. S.; Scholz, W. F.; Lee, Y. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 2644.

(3) Song, H.; Reed, C. A.; Scheidt, W. R. *J. Am. Chem. Soc.* **1989**, *111*, 6865.

(4) (a) Reddy, D.; Chandrashekar, T. K. *J. Chem. Soc., Dalton Trans.* **1992**, 619. (b) Three isomers. Cross trans linked, adjacent trans linked, and adjacent cis linked have been isolated. See ref 4a for the details of the structures.

(5) Reddy, D.; Chandrashekar, T. K.; vanWilligen, H. *Chem. Phys. Lett.* **1993**, *202*, 120.

(6) Ravikanth, M.; Reddy, D.; Chandrashekar, T. K. *J. Photochem. Photobiol. A: Chem.* **1993**, *72*, 61.

(7) Ravikanth, M.; Chandrashekar, T. K. *J. Photochem. Photobiol. A: Chem.*, in press.

(8) Ravikanth, M.; Reddy, D.; Misra, A.; Chandrashekar, T. K. *J. Chem. Soc., Dalton Trans.* **1993**, 1137.

(9) Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 6791.

(10) Weiner, S. J.; Kollman, P. A.; Case, D. A.; Singh, U. C.; Ghio, C.; Alagona, G.; Profeta, Jr. S.; Weiner, P. *J. Am. Chem. Soc.* **1984**, *106*, 765.

0020-1669/94/1333-0392$04.50/0

Table I. Comparison of Resonance Raman Frequencies (cm^{-1}) of Cu((PSI)Br$_8$) and CuHexylI and Their Cation Radicals with CuTPP and Its Cation Radical

mode no.	description	CuTPP^a	[CuTPP][SbCl$_6$]^a	Cu((PSI)Br$_8$)	[Cu((PSI)Br$_8$)][SbCl$_6$]	CuHexylI	[CuHexylI][SbCl$_6$]
ν_ϕ	ν_{C-C} phenyl	1599	1595	1605	1577	1607	1583
ν_2	$\nu(C_\beta-C_\beta)_{sym}$	1562	1530	1553	1545	1557	1547
ν_{11}	$\nu(C_\beta-C_\beta)_{asym}$	1501		1480		1485	
ν_4	ν(Pyr half ring)$_{sym}$	1365	1355	1370	1361	1370	1357
ν_1	$\nu(C_m-C_\phi)$	1237	1234	1245	1256	1245	1252
ν_9	$\delta(C_\beta-H)_{sym}$	1080	1077	1074	1072	1079	1072
ν_6	ν(Pyr breathing)	1008	1002	1024	1005	1023	1002
ν_7	δ(Pyr def)$_{sym}$	886	884	900	905	911	923

^{a} Data taken from ref 22.

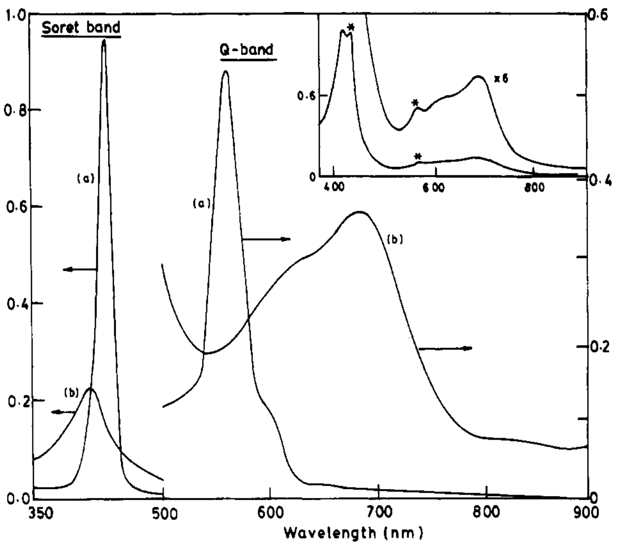

Figure 2. Comparison of the optical absorption spectra of (a) Cu((PSI)-Br$_8$) and (b) [Cu((PSI)Br$_8$)][SbCl$_6$] in CH$_2$Cl$_2$. The concentrations used were $\simeq 2 \times 10^{-5}$ mol dm^{-3} for Q bands and $\simeq 2 \times 10^{-6}$ mol dm^{-3} for Soret band. The inset shows the optical spectra of coulometrically oxidised species of Cu((PSI)Br$_8$). An asterisk indicates the presence of some unoxidized Cu((PSI)Br$_8$).

CH$_2$Cl$_2$ generates crystalline radical cations.[2,9] A comparison of optical spectra of neutral Cu((PSI)Br$_8$) with its π-cation radical in CH$_2$Cl$_2$ is shown in Figure 2. The electrochemically generated optical spectra of Cu((PSI)Br$_8$)$^{\bullet+}$ by controlled-potential coulometry at +0.96 V in CH$_2$Cl$_2$ with 0.1 M TBAP is included in inset. Broad, featureless red-shifted Q-bands and blue-shifted Soret band with reduced extinction coefficients of the oxidized species are in conformity with the oxidation of the ring.[11,12] Further confirmation of ring oxidation comes from the solid-state IR data in KBr pellets where the diagnostic π-cation radical band around 1285 cm^{-1} was observed in all the cases.[13]

Resonance Raman spectra of Cu((PSI)Br$_8$) and CuHexylI and their corresponding cation radicals in CH$_2$Cl$_2$ in the region 800–1800 cm^{-1} are recorded, and the frequencies of important modes are listed in Table I. The assignments of important vibrational modes are done following the recent work of Spiro and co-workers.[14] The following changes were noted upon the comparison of neutral derivatives with the corresponding π-cation radicals: (a) ν_2 and ν_4 modes shift to lower frequency and the magnitude of shifts vary from 10 to 30 cm^{-1}. (b) ν_1 shifts to the higher frequency ($\simeq$10 cm^{-1}) while ν_9 shifts to lower frequency ($\simeq$7 cm^{-1}). (c) The relative intensities of the Raman bands also change; for example the ν_ϕ gains intensity while ν_2 and ν_4 modes lose intensity.

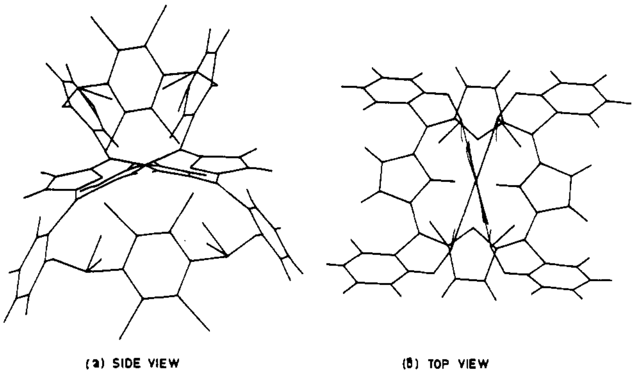

Figure 3. Energy-optimized calculated structure of (PSI)Br$_8$.

The oxidized products were found to be EPR silent both in solid and CH$_2$Cl$_2$ over a temperature range 300–70 K, suggesting the diamagnetic nature of the oxidized species. This was confirmed by variable-temperature magnetic susceptibility measurements over the range 300–80 K. Repeated magnetic susceptibility measurements (Evans method)[15] in CD$_2$Cl$_2$ at 300 K indicate a small magnetic moment of 0.235 μ_β. This value may be contrasted with 2.4 μ_β measured for CuTPP$^{\bullet+}$ in CD$_2$Cl$_2$ at 300 K.[2,9]

Figure 3 gives the calculated structure of the (PSI)Br$_8$ using the MOBY geometry optimization program. The computation of energy according to the classical force field is based on the AMBER[10] force field. It has been possible to calculate the structures of all the isomers,[4] and the details of the structure will be published elsewhere separately. In the present context, the calculated structure is shown only to highlight the existence of severe deformation in the porphyrin core.

Discussion

Shelnutt,[16,17] Birkigia,[18] and co-workers have recently related the magnitude of optical absorption red shifts to the degree of nonplanarity from a combination of INDO/CI molecular orbital calculations and experimental results on a series of highly nonplanar porphyrins.[16–18] It has been shown that the HOMO is destabilised upon distortion of the porphyrin core resulting in the decrease of the energy gap between the HOMO and LUMO which is spectroscopically manifested in the optical absorption red shifts. A comparison of the absorption maxima of CuTPP$^{\bullet+}$ (630, 600 (sh), 408 nm) with the Cu((PSI)Br$_8$)$^{\bullet+}$, CuHexylI$^{\bullet+}$, Cu((MSI)Cl$_8$)$^{\bullet+}$, and CuPSI$^{\bullet+}$ suggests considerable (1370, 485, 238; 1254, 380, 119; 1608, 355; 1296, 273, 355 cm^{-1}, respectively) red shifts of Q and Soret bands in the basket-handle porphyrin radical cations, suggesting the presence of deformation in the solution.

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(11) Fajer, J.; Davis, S. *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979, Vol. 4, p 198.

(12) Edwards, W. D.; Zerner, M. C. *Can. J. Chem.* **1985**, *63*, 1763.

(13) Shimomura, E. T.; Philippi, M. A.; Goff, H. M.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6778.

(14) Li, X. Y.; Czernuszewicz, R. S.; Kincaid, J. R.; Su, O.; Spiro, T. G. *J. Phys. Chem.* **1990**, *94*, 31.

(15) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(16) Sparks, L. D.; Medforth, C. J.; Park, M. S.; Chamberlain, J. R.; Ondrias, M. R.; Senge, M. O.; Smith, K. M.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 581.

(17) Shelnutt, J. A.; Medforth, C. J.; Berber, M. D.; Birkigia, Smith, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 4077.

(18) Birkigia, K. M.; Chantranupong, L.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1988**, *110*, 7566.

An analysis of the calculated structures of the basket-handle porphyrins reveal the enforced deformation in the porphyrin skeleton by covalent attachment of the short bridging chain. Furthermore, because the chains are linked at the ortho position of the meso phenyl rings, the dihedral angle[19] between the phenyl rings and the porphyrin plane is reduced making the phenyl rings more coplanar with the porphyrin plane facilitating the delocalisation of π-electrons in to the phenyl rings. This effect is clearly reflected in shifts of porphyrin skeletal modes ν_2 and ν_{11} to lower frequencies relative to planar CuTPP (Table I).[20]

The direction of the shifts of the porphyrin skeletal modes upon radical formation are suggested to be diagnostic of the predominant orbital character (a_{1u} and a_{2u})[20]. The shift of ν_2 mode, which involve C_β–C_β stretching mainly and some contribution from C_α–C_m to lower frequencies suggest the abstraction of electron from an a_{2u} orbital since a_{2u} orbital is bonding with respect to both these bonds. The nature of the absorption spectra of (Figure 2) also supports this conclusion.[12,21] The 13-cm^{-1} shift of the ν_4 mode assigned to the pyrrole symmetric half-ring stretch to lower frequency is consistent with the observed 4–18-cm^{-1} lower frequency shifts for many MTPP radical cations having an a_{2u} ground state.[22]

The observed small (5–7 cm^{-1}) higher frequency shifts of phenyl mode (ν_ϕ) in the neutral derivatives relative to CuTPP further reflects the strengthening of the C-C bond of meso phenyl rings via the extended π-delocalization. However, the large shift (20–25 cm^{-1}) to lower frequencies of the ν_ϕ mode upon radical formation suggests the disruption in the delocalization pathway.[19,22] The intensity increase in the phenyl modes in the π-cations is attributed to phenyl porphyrin mode mixing, and it has been shown earlier that such mixing between ν_2 and ν_ϕ modes are possible due to the favorable orientation of coordinates.[14]

Previous magnetic studies on the CuTPP$^{\bullet+}$ radical indicates that the radical cation is completely diamagnetic in the solid state and paramagnetic ($S = 1$) in solution.[2,9,23] The diamagnetism in the solid state was explained on the basis of an X-ray crystal structure of the radical cation.[2,9] An important feature of the solid-state structure is the appearance of tightly associated pairs of cations with a Cu--Cu separation of 5.43 Å. Furthermore, because of the ruffled core, the orthogonality of the ligand a_u and metal $d_{x^2-y^2}$ magnetic orbitals are destroyed, providing a pathway for intramolecular d–π coupling within each CuTPP$^{\bullet+}$ molecule accounting for the observed diamagnetism. In solution, however it was assumed that CuTPP$^{\bullet+}$ is monomeric with a planar core where strict orthogonality of magnetic orbitals prevents the d–π coupling, giving rise to the paramagnetic state. The X-ray structure of [CuTMP][SbCl$_6$] is in conformity with this argument.[3]

However, for the porphyrins described here, dimer formation is completely ruled out because of the bridging chain above and below the porphyrin plane. Thus, the observed diamagnetism has to be explained in terms of the deformation of the porphyrin core caused by attachment of the short bridging chain. This deformation can be compared to the so-called ruffling of the porphyrin core in which opposite pyrrole rings are alternatively displaced up and down relative to the mean plane.[1] The calculated structure (Figure 3) clearly displays this ruffling. The effect of this ruffling is to remove the orthogonality between the metal $d_{x^2-y^2}$ orbital and the porphyrin $a_u(\pi)$ orbital, allowing the intramolecular d–π coupling necessary for antiferromagnetic exchange.[2] Furthermore, the observed diamagnetism in solution also should be attributed to antiferromagnetic coupling unlike in CuTPP$^{\bullet+}$. This is possibe only when the ruffling is retained in solution, since it is well established that the planar porphyrin cores lead to ferromagnetic coupling.[2,3] This clearly suggests that the bridging chain across the porphyrin periphery prevents the flexibility of the molecule to interconvert between the ruffled to planar core on going from solid state to solution state as observed for CuTPP$^{\bullet+}$. Thus, in conclusion, the present study is important from the following two observations: (a) the ruffling in the present structures is due to covalent attachment of short bridging chain across the porphyrin periphery and not due to dimerization, and (b) to the best of our knowledge most of the copper *meso*-arylporphyrin π-cation radicals reported to date are paramagnetic in solution and this is the only report where diamagnetism has been observed in solution.

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(19) Ravikanth, M.; Misra, A.; Chandrashekar, T. K. *J. Chem. Soc., Dalton Trans.*, in press.

(20) (a) Spiro, T. G.; Czernuszewicz, R. S.; Li, X. Y. *Coord. Chem. Rev.* **1990**, *100*, 541. (b) Further support for this conclusion comes from the decrease in the zero field splitting parameter (*D*) relative to H$_2$TPP in the photoexcited triplet ESR spectra of PS1. Please see ref 5 for details.

(21) Dolphin, D.; Muljiani, Z.; Rousseau, K.; Borg, D. C.; Fajer, J.; Felton, R. H. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 177.

(22) Czernuszewicz, R. S.; Macor, K. A.; Li, X. Y.; Kincaid, J. R.; Spiro, T. G. *J. Am. Chem. Soc.* **1989**, *111*, 3860.

(23) Godziela, G. M.; Goff, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 2237.