Table I. Values for the Enzymatic Acylation of Subtilisin and α-Chymotrypsin by a Series of Para-Substituted Phenyl Acetates in Various Solvents[a]

enzyme[b]	solvent[c]	ρ[d]	ref
subtilisin	water	0.87	this work
subtilisin	tetrahydrofuran	0.86	this work
subtilisin	acetone	0.93	this work
subtilisin	butyl ether	0.91	this work
subtilisin	acetonitrile	0.72	this work
subtilisin	*tert*-amyl alcohol	0.83	this work
α-chymotrypsin	water	1.8	*e*
α-chymotrypsin	water	1.8	ref 17
α-chymotrypsin	water	2.1	*f*
α-chymotrypsin	water	1.9	*g*

[a] For experimental conditions, see the legend to Figure 1. [b] Subtilisin was obtained, prepared, and used as previously described (ref 6). We established that the enzyme irreversibly inactivated by the active center-directed inhibitor phenylmethanesulfonyl fluoride (Fahrney, D. E.; Gold, A. M. *J. Am. Chem. Soc.* **1963**, *85*, 997-1000) was completely inactive in organic solvents; hence the transesterification reactions observed and their ρ values correspond to the molecular events occurring in subtilisin's active center. [c] All nonaqueous solvents were dried to bring the water content below 0.01% (measured as described in ref 6). [d] All ρ values are determined using σ^- substituent constants, as had been done in the four studies of chymotryptic hydrolysis in water depicted at the bottom of the table. [e] Bender, M. L.; Nakamura, K. *J. Am. Chem. Soc.* **1962**, *84*, 2577-2582. [f] Hubbard, C. D.; Shoupe, T. S. *J. Biol. Chem.* **1977**, *252*, 1633-1638. [g] Ikeda, K.; Kunugi, S.; Ise, N. *Arch. Biochem. Biophys.* **1982**, *217*, 37-46.

water-miscible (acetone, tetrahydrofuran, and acetonitrile) and differ widely in terms of their hydrophobicity[12] and polarity;[13] and yet, all the ρ values fall within less than a ±15% range (Table I). Therefore, given the substantial error inherent in the experimental determination of this reaction constant,[11] it can be concluded that the ρ value for the subtilisin-catalyzed cleavage of phenyl acetates is essentially independent of the nature of the solvent.

It should be stressed that the value of ρ, which reflects the charge distribution in the transition state, is very sensitive to even subtle changes in the mechanism of chemical processes in general,[1,11] and subtilisin catalysis in particular. With respect to the latter, two examples are particularly indicative. First, the ρ value for subtilisin-catalyzed hydrolysis (in aqueous solutions) drops almost 4-fold when substituted phenyl hippurates are used as substrates instead of substituted phenyl acetates.[14] Second, when subtilisin is replaced with the closely related[15] serine protease α-chymotrypsin as a catalyst, the ρ value for the hydrolysis of phenyl acetates in water more than doubles (Table I). Comparison of these results with our data suggests that the structure of the transition state formed upon acylation of subtilisin with phenyl acetates is substantially the same regardless of the solvent.

The ρ values for the (nonenzymatic) alkaline hydrolysis of substituted phenyl acetates (as well as for other chemical processes[1,11]) strongly depend on the reaction medium, e.g., upon a transition from water to 62% aqueous acetone the reaction constant increases from 0.66-0.71 to 1.14;[16] presumably, an even greater change would be observed for more concentrated acetone solutions. In contrast, the ρ values for subtilisin-catalyzed cleavage of phenyl acetates in water and in neat tetrahydrofuran and *tert*-amyl alcohol are virtually identical (Table I). These data suggest that the microenvironment of the transition state of the enzymatic reaction is the same for the three solvents, i.e., that the enzyme's active center is shielded from the bulk solvent. Overall, the results of this study indicate profound mechanistic similarities of subtilisin catalysis in water and various organic solvents.

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(12) Log *P* (where *P* is the logarithm of the partition coefficient between 1-octanol and water) for the solvents used varies from −0.33 for acetonitrile to +2.9 for butyl ether (Laane, C.; Boeren, S.; Vos, K.; Veeger, C. *Biotechnol. Bioeng.* **1987**, *30*, 81-87).

(13) For example, the dielectric constant and dipole moment, respectively, vary from 5.8 and 1.7 for *tert*-amyl alcohol to 36 and 3.9 for acetonitrile (Gordon, A. L.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972; pp 2-13).

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Metalloporphyrin π-Cation Radicals: Intrinsically Ruffled or Planar Core Conformations? Molecular Structure of (Mesitylporphinato)copper(II) Hexachloroantimonate

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Metalloporphyrin π-cation radicals are important in the redox chemistry of a variety of biological systems including heme catalysis and photosynthesis. Our groups have recently been concerned with their structural characterization with special emphasis on understanding their magnetic properties.[3,4] Spin coupling mechanisms between the porphyrin radical and unpaired electrons at the metal are exquisitely sensitive to structure. Ruffled porphinato cores lead to antiferromagnetic coupling, whereas planar cores show ferromagnetic coupling, a phenomenon that can be understood from inspection of the symmetries of the magnetic orbitals. Although all structurally characterized species follow this correlation, the full characterization of a pair of π-cation derivatives that have the same metal and ligation state but which individually display magnetic properties characteristic of the two coupling modes has remained elusive.

One key structural question that has arisen from the studies to date is whether the S_4-ruffled porphinato core observed in all previously structurally characterized four- and five-coordinate π-cation complexes is an intrinsic structural property of these molecules. We have suggested that the unusual saddle-shaped S_4-ruffled porphinato core[5] observed in the π-cation radical species is a necessary molecular distortion required to allow dimerization and not an intrinsic property resulting from some distinctive electronic state of the π-cation. This argument is supported by the observation of the same type of conformation in a number of neutral tetraphenylporphyrin derivatives, all of which exhibit a π–π dimer interaction in the solid state.[6] In this communication and the following one, we present the structural characterization of two metalloporphyrin π-cation radicals that we believe conclusively resolve this issue. The present paper reports the solid-state structure of $[Cu(TMP^{\bullet})]SbCl_6$,[7] the long sought ferromagnetically

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(3) Gans, P.; Buisson, G.; Duée, E.; Marchon, J.-C.; Erler, B. S.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 1223.

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(5) There are two types of idealized S_4 (D_{2d})-ruffled core conformations in porphyrin complexes. These differ by a rotation of the symmetry elements by 45° about the axis normal to the plane. Thus, the methine carbons (C_m) are either alternately above and below the porphyrin plane or are on the mean porphyrin plane. The former conformation is more common; the latter has the saddle-shaped surface described for the π-cation species with both β-carbon atoms of the pyrrole rings alternatively above or below the mean plane of the 24-atom core.

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

(7) Abbreviations used: TMP, dianion of tetramesitylporphyrin; $TMP^{\bullet}$, singly oxidized (π-cation) form of TMP; TPP, dianion of tetraphenylporphyrin; $TPP^{\bullet}$ singly oxidized (π-cation) form of TPP.

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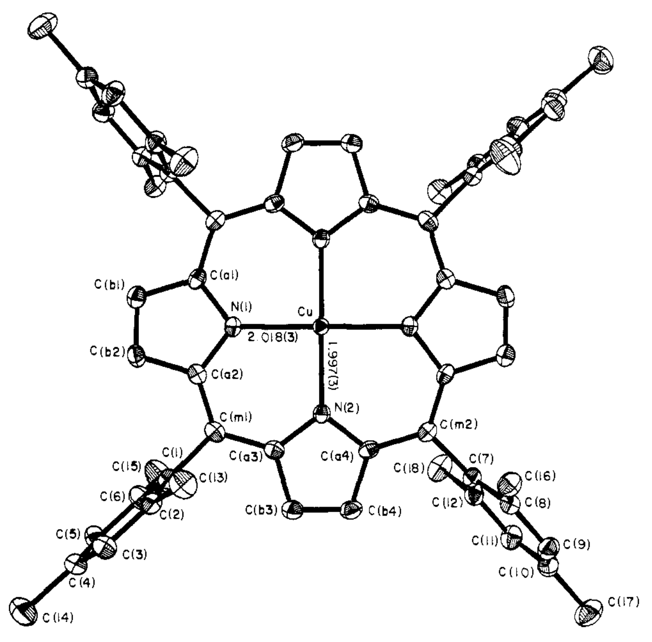

Figure 1. ORTEP drawing of an individual molecule of [Cu(TMP$^\bullet$)]SbCl$_6$ as it exists in the crystal. The molecule has crystallographically required inversion symmetry with the center at the copper(II) ion.

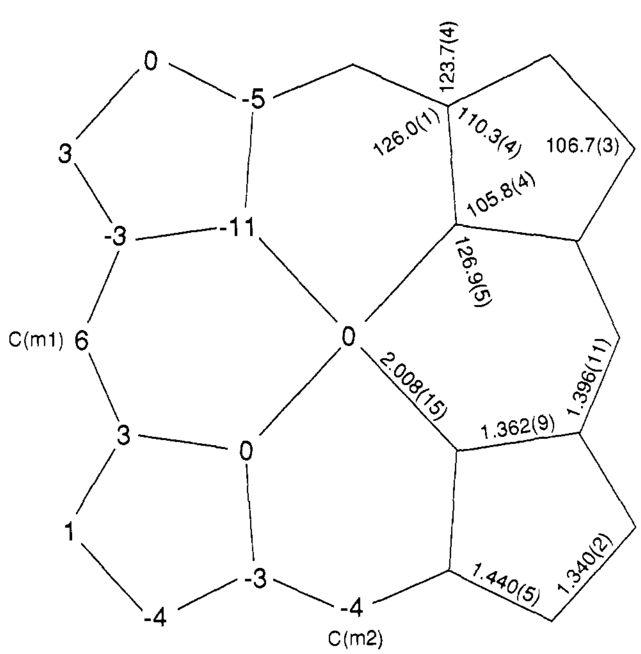

Figure 2. Formal diagram of the core in [Cu(TMP$^\bullet$)]SbCl$_6$ illustrating deviations (in units of 0.01 Å) of the unique atoms from the mean plane of the core and the averaged bond parameters.

coupled partner of the antiferromagnetically coupled [Cu(TPP$^\bullet$)]SbCl$_6$.[4] The *o*-methyl substituents on the TMP ligand were expected to provide adequately bulky peripheral substituents to prevent the type of $\pi-\pi$ solid-state aggregation seen in the TPP derivatives.

[Cu(TMP$^\bullet$)]SbCl$_6$ was prepared by oxidation of Cu(TMP)[4,8] with tris(4-bromophenyl)aminium hexachloroantimonate and recrystallized from dichloromethane/hexane. As reported previously,[4] the complex displays an IR band (1280 cm^{-1}) that is diagnostic for radical formation. The molecular structure of [Cu(TMP$^\bullet$)]SbCl$_6$ has been determined by X-ray crystallography[9] and is illustrated in Figure 1. An important feature of the molecular structure is that the planes of the peripheral mesityl groups are nearly perpendicular to the mean plane of the porphinato core[10] and inhibit approach of a second radical. Thus, the expectation of monomeric cations has been realized. The Cu···Cu separation is 9.30 Å (with a precisely intervening SbCl$_6^-$ anion), and the closest intermolecular porphyrin ring atom-to-ring approach is >6.7 Å. The copper(II) ion is precisely centered in the porphinato plane, and the 24-atom core is nearly planar. The requirement of a crystallographic inversion center at copper excludes the possibility of S$_4$ ruffling. Figure 2 is a formal diagram of the porphinato core that displays the perpendicular displacements (in units of 0.01 Å) of each crystallographically unique atom from the best plane of the 24-atom core. The pattern clearly retains no vestige of the saddle-shaped cores of the dimeric TPP derivatives. Figure 2 also displays the averaged values for all bond parameters in the core. These core bond distances follow closely those of several neutral copper(II) porphyrins[11] and that of the [Cu(TPP$^\bullet$)]SbCl$_6$ radical.[4] The average Cu–N distance of 2.008 (15) Å is the value expected for a planar derivative.

It is important to note that although the use of a mesitylporphyrin derivative does prevent dimer formation it does not prevent the porphinato core from having a saddle-shaped surface.[12] We thus interpret the planarity of the porphyrin core in this TMP$^\bullet$ derivative as clearly showing that the unusual saddle-shaped core conformation previously found for several tetraaryl π-cation derivatives is not an intrinsic conformational aspect of π-cations but rather is a consequence of *dimer* formation in *tetraaryl* derivatives.

The magnetic moment of [Cu(TMP$^\bullet$)]SbCl$_6$·CH$_2$Cl$_2$ is significantly in excess of the value expected for noninteracting spins and is essentially temperature independent (2.6 ± 0.1 μ_B from 6–300 K).[13] This is consistent with the conclusion of strong intramolecular ferromagnetic coupling previously found in the fluorobenzene solvate[4] and is rationalized by orthogonality of the copper and ring magnetic orbitals in the nearly D_{4h} symmetry of isolated [Cu(TMP$^\bullet$)]$^+$ ions. It constrasts sharply with the diamagnetism of the S_4-ruffled TPP$^\bullet$ analogue and provides an essential proof for the magnetic interaction hypothesis advanced in earlier papers.[3,4]

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Supplementary Material Available: Table IS, atomic coordinates, and Tables IIS and IIIS, complete tables of bond distances and angles, for [Cu(TMP$^\bullet$)]SbCl$_6$, and Table IVS, anisotropic thermal parameters (6 pages); listing of observed and calculated structure factors (×10) (18 pages). Ordering information is given on any current masthead page.

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(8) Wagner, R. W.; Lawrence, D. S.; Lindsey, J. *Tetrahedron Lett.* **1987**, *28*, 3069.

(9) Although [Cu(TMP$^\bullet$)]SbCl$_6$ crystallizes readily in our laboratory, adequate diffraction quality crystals of [Cu(TMP$^\bullet$)]SbCl$_6$ are obtained with difficulty. Crystals of [Cu(TMP$^\bullet$)]SbCl$_6$ crystallize as the dichloromethane solvate in the tetragonal system, CuSbCl$_6$N$_4$C$_{56}$H$_{52}$·CH$_2$Cl$_2$, space group $P4_2/n$, a = 25.038 (15) Å, c = 9.302 (13) Å, and Z = 4. A total of 15 593 data were measured in two equivalent forms of which 7396 were unique. The two sets were averaged and gave 4546 observed averaged data out to 2θ of 56.9° (merging R = 0.052 on I). These data were collected by θ–2θ scanning on an Enraf-Nonius CAD4 diffractometer at 118 K. The structure was solved from a Patterson map and the direct methods program DIRDIF. Least-squares refinement of the model based on 355 variables with anisotropic thermal parameters for all non-hydrogen atoms and fixed, idealized hydrogen atom contributors leads to R_1 = 0.043 and R_2 = 0.053.

(10) This is distinctly different than the tetraryl dimer species where the dihedral angle between aryl substituents and porphyrin core are quite small (<55°). In [Cu(TMP$^\bullet$)]SbCl$_6$, the actual dihedral angles are 84.3 and 79.0°.

(11) Fleischer, E. B.; Miller, C. K.; Webb, L. E. *J. Am. Chem. Soc.* **1964**, *86*, 2342. Moustakali, I.; Tulinsky, A. *J. Am. Chem. Soc.* **1973**, *95*, 6811. Collman, J. P.; Chong, A. O.; Jameson, G. B.; Oakley, R. T.; Rose, E.; Schmittou, E. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 516. Fillers, J. P.; Ravichandran, K. G.; Abdalmuhdi, I.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 417. Hatada, M. H.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1980**, *102*, 7116.

(12) Such a porphinato core surface, with three nearly perpendicular phenyl groups, has been described for one crystalline polymorph of neutral CoTPP. See Table XXIV of ref 6 for complete details. Sato, M.; Kon, H.; Akoh, H.; Tasaki, A.; Kabuto, C.; Silverton, J. V. *Chem. Phys.* **1976**, *16*, 405. Dr. Kon kindly provided atomic coordinates.

(13) Experimental methods are as reported earlier.[4]