Dimerization of Metalloporphyrin π-Cation Radicals. $[Zn(OEP^{\bullet})(OH_2)]_2(ClO_4)_2$, a Novel Dimer

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The key issues concerning the stereochemistry of tetraarylporphyrin π-cation radicals have been addressed in the preceding communication. In this communication we report the preparation, crystal structure determination, and magnetic properties of dimeric $[Zn(OEP^{\bullet})(OH_2)]ClO_4$.[3] Although OEP π-cation radicals have been known for some time,[4] there are no reported crystal structures for this class; all previously reported structures have utilized meso-substituted tetraaryl derivatives. However, the OEP derivatives represent an interesting class of ligands in which the peripheral groups are decidedly nonbulky and thus will provide minimum impedance toward the formation of dimers or extended aggregates in the solid state. The importance of this molecular feature is emphatically seen in the structure of $[Zn(OEP^{\bullet})(OH_2)]_2(ClO_4)_2$ which forms an extremely tight π–π dimer with several novel features.

$[Zn(OEP^{\bullet})(OClO_3)]$ was prepared by chemical oxidation of Zn(OEP) with thianthrenium perchlorate. Crystallization from dichloromethane/hexane apparently yields an anhydrous complex, while crystallization from 1,2-dichloroethane/hexane yields an aquated dimeric species, $[Zn(OEP^{\bullet})(OH_2)]_2(ClO_4)_2$.[5,6] The IR spectra (KBr) of these materials are similar to that reported[7] for $[Zn(OEP^{\bullet})Br]$ but differs from that reported[8] for $[FeCl(OEP^{\bullet})]SbCl_6$. The strong π-cation radical marker band[9] of the latter appears only as two weak bands at 1530 and 1555 cm^{-1} in $[Zn(OEP^{\bullet})(OH_2)]_2(ClO_4)_2$. A number of other bands in $[Zn(OEP^{\bullet})(OH_2)]_2(ClO_4)_2$ also appear to be doublets. An infrared trace (KBr pellet) is given in the Supplementary Material.

The molecular structure of the monomeric unit, $[Zn(OEP^{\bullet})(OH_2)]ClO_4$, is shown in Figure 1. The molecule has a crystallographically imposed 2-fold axis along the Zn–OH_2 axis. Although the imposed symmetry of the molecule does not lead to any conditions on the planarity of the porphinato core, the molecule is essentially planar with the largest deviation of any atom from the mean plane of the 24-atom core equal to 0.05 Å. The Zn–N_p bond distances average to 2.051 (3) Å, and the axial Zn–O bond distance is 2.141 (3) Å. Although the axial distance is a normal distance for five-coordinate zinc species[10] with a neutral porphyrin ligand, the Zn–N_p distances are significantly shorter. Moreover, the displacement of the zinc(II) atom from the mean

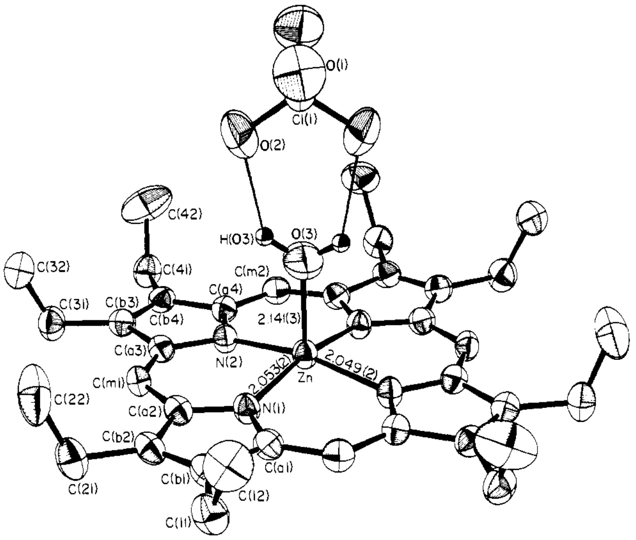

Figure 1. ORTEP drawing of an individual unit of $[Zn(OEP^{\bullet})(OH_2)]_2(ClO_4)_2$ as it exists in the crystal. The Zn, water O, and perchlorate Cl are located on the crystallographic 2-fold axis.

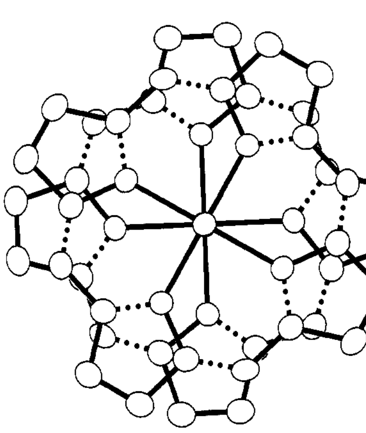

Figure 2. ORTEP drawing illustrating the cofacial dimer found in crystals of $[Zn(OEP^{\bullet})(OH_2)]_2(ClO_4)_2$. The view is down a 2-fold axis of symmetry. Average C_a–N bond distances are 1.342 (5) or 1.384 (5) Å and average C_a–C_m distances are 1.372 (3) or 1.416 (2) Å. The short bonds of each type are shown as broken lines; the long bonds are given as full bonds. The peripheral ethyl groups have been omitted for the sake of clarity.

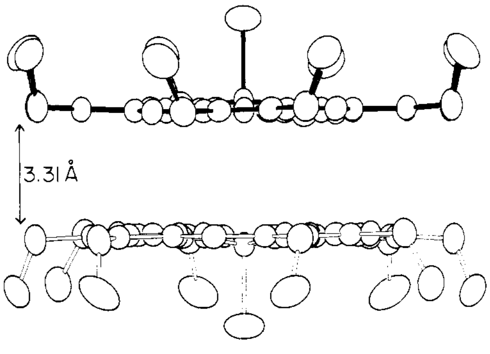

Figure 3. Edge-on view of the cofacial dimer illustrating the essential planarity of the two rings within the dimer.

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[3] Abbreviations used: OEP, dianion of octaethylporphyrin; $OEP^{\bullet}$, singly oxidized (π-cation) form of OEP; TPP, dianion of tetraphenylporphyrin.

[4] (a) Fuhrhop, J.-H.; Mauzerall, D. *J. Am. Chem. Soc.* **1969**, *91*, 4174. (b) Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *Ibid.* **1970**, 3451. (c) Fuhrhop, J.-H.; Wasser, P.; Riesner, D.; Mauzerall, D. *Ibid.* **1972**, *94*, 7996.

[5] We have observed that a number of π-cation porphyrin species have high affinity for an aquo ligand and are easily aquated by the small amount of water found even in carefully dried solvents. Halocarbon solvents such as 1,2-dichloroethane and 1,1,2,2-tetrachloroethane appear exceptionally difficult to dry sufficiently to avoid formation of the aquated radicals. We note that such aquo ligation is likely to be especially troublesome in dilute solution or low-temperature experiments.

[6] $[Zn(OEP^{\bullet})(OH_2)]ClO_4$ crystallizes as the 1,2-dichloroethane solvate in the orthorhombic system, $ZnCl_3O_4N_4C_{38}H_{48}$, space group *Fddd*, $a = 29.126$ (5) Å, $b = 34.956$ (7) Å, $c = 15.670$ (3) Å, and $Z = 16$. A total of 3924 observed data out to 2θ of 54.9° were collected by θ–2θ scanning on a Nicolet P$\bar{1}$ diffractometer. The structure was solved with the direct methods program DIRDIF. Least-squares refinement of the model based on 233 variables with anisotropic thermal parameters for all non-hydrogen atoms and fixed, idealized hydrogen atom contributors converged at $R_1 = 0.051$ and $R_2 = 0.051$.

[7] Itoh, K.; Nakahasi, K.; Taeda, H. *J. Phys. Chem.* **1988**, *92*, 1464.

[8] Gans, P.; Buisson, G.; Duēe, E.; Marchon, J.-C.; Erler, B. S.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 1223.

[9] Shimomura, E. T.; Phillippi, M. A.; Goff, H. M.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6778.

[10] Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3761. Cullen, D. L.; Meyer, E. F., Jr. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2259. Bobrik, M. A.; Walker, F. A. *Inorg. Chem.* **1980**, *19*, 3383. Hatano, Kawasaki, K.; Munakata, S.; Iitaka, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1992. Brennan, T. D.; Scheidt, W. R. *Acta Crystallogr., Sect. C* **1988**, *C44*, 478.

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plane of the porphinato core is 0.24 Å, a value smaller than that typically observed in five-coordinate zinc porphyrinates.[10] This smaller zinc displacement is probably the result of the interaction of one monomeric unit with its cofacial partner (see below). As noted previously, the effect of π-complexation[11] or π–π dimer formation[12] on the metal atom position with respect to the porphyrin plane is somewhat equivalent to that of a weakly interacting sixth ligand. The effect of $\mathrm{[Zn(OEP^{\bullet})(OH_2)]_2(ClO_4)_2}$ is relatively large and is the presumed consequence of the extremely strong dimerization. It is presumably the effects of dimer formation that also lead to the relatively short $\mathrm{Zn–N_p}$ bonds that are close to the 2.037-Å value found for four-coordinate Zn porphyrinates[13] rather than the 2.067 Å found[10] for the five-coordinate Zn(P)L complexes.

In the solid state, $\mathrm{[Zn(OEP^{\bullet})(OH_2)]_2(ClO_4)_2}$ is a cofacial π–π dimer with several significant and novel features. First, the two porphyrin rings in the dimer interact in an exceptionally strong manner with an interplanar separation between the two porphyrin planes of 3.31 Å. Perhaps not surpisingly, the crystalline material is diamagnetic.[14] Second, the absence of any lateral shift between the two cofacial porphyrin rings is unprecedented.[15] Previously characterized, extremely tight π–π dimeric interactions between two rings exhibit lateral shifts of about 1.5 Å or larger.[16] The absence of ring slip is illustrated in Figure 2 which shows a view down the crystallographic 2-fold axis of one unit and clearly shows the overall high symmetry of the dimer. The *dimer* has crystallographically required D_2-222 symmetry but additionally conforms to the higher idealized symmetry of D_{2d}. Third, despite the strong interaction between rings, the rings are essentially planar as seen in Figure 3. Fourth, the pattern of bond distances in the inner 16-membered ring of the porphyrin core are inconsistent with a completely delocalized system. Rather, there are two unusually distinct sets of $\mathrm{C_a–N}$ and $\mathrm{C_a–C_m}$ bond distances.[17] Within each class, the two kinds of bond lengths differ by about 0.04 Å. The position of the sets of short bonds in the dimer are indicated in Figure 2 by the broken bonds. It is clearly seen that all short bonds are within overlapped pyrrole rings. This apparent localization of bonding[18] is presumably due to the effects of dimerization whose tightness and spin coupling suggests a new kind of interaction, best described as a new type of nonclassical bond. Indeed, the large enthalpy of dimerization (−17 kcal/mol), significant spectral changes upon dimerization,[4c] and complete loss of paramagnetism from the radical are consistent with the notion of forming a new compound. Interestingly, it can be noted that similar spectral changes have been seen upon dimerization (in solution) of the $\mathrm{[Mg(OEP^{\bullet})]^+}$ radical cation.[4b,19]

The question of whether this unprecedented departure from complete delocalization in porphyrin derivatives is a general feature of tightly bonded π-cation dimers is under active investigation. In any event, these bond length changes present an interesting and challenging theoretical problem. We can note that the alternating bond distances do not result simply from bringing two porphyrin rings extremely close together. A similar inter-ring separation and ring orientation is found in the $\mathrm{[Ru(OEP)]_2}$ dimer[20] held together by the short Ru=Ru double bond, but no bond length alternation in the core is observed.

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Supplementary Material Available: Figure 1S, infrared spectrum, Table IS, complete atomic coordinates, Tables IIS and IIIS, complete tables of bond distances and angles for $\mathrm{[Zn(OEP^{\bullet})(OH_2)]_2(ClO_4)_2}$, Table IVS, anisotropic thermal parameters, and Table VS, magnetic data (7 pages); listing of observed and calculated structure factors (×10) (13 pages). Ordering information is given on any current masthead page.

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[11] Williamson, M. M.; Hill, C. L. *Inorg. Chem.* **1987**, *26*, 4155.

[12] Song, H.; Rath, N. P.; Reed, C. A.; Scheidt, W. R. *Inorg. Chem.* **1989**, *28*, 1839.

[13] Scheidt, W. R.; Kastner, M. E.; Hatano, K. *Inorg. Chem.* **1978**, *17*, 706. Scheidt, W. R.; Mondal, J. U.; Eigenbrot, C. W.; Adler, A.; Radonovich, L. J.; Hoard, J. L. *Inorg. Chem.* **1986**, *25*, 795.

[14] The raw magnetic susceptibility data are given in the Supplementary Material and show the presence of less than 1% paramagnetic impurity.

[15] However, such a cofacial structure was one of two possible structures suggested by Fuhrhop et al.,[4c] and the one they considered most probable.

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

[17] A complete listing of individual bond distances and angles in the $\mathrm{[Zn(OEP^{\bullet})(OH_2)]ClO_4}$ molecule are available as Supplementary Material.

[18] This localization may be reflected in the doubling of peaks in the IR spectrum. (See spectrum in Supplementary Material.)

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

[20] Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500.

Evidence for a 1,2-Fluoride Shift in a Gaseous Cation

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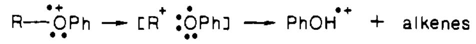
Bond heterolysis of a gaseous ion to form an ion–molecule complex (exemplified by the species in brackets shown in reaction 1) has been described as a gas-phase analogue of solvolysis.[1]



$$\mathrm{R{-}\overset{\bullet +}{\underset{\bullet\bullet}{O}}Ph \longrightarrow [R^{+}\ {:}\overset{\bullet}{\underset{\bullet\bullet}{O}}Ph] \longrightarrow PhOH^{\bullet +} + alkenes} \qquad (1)$$

Conversion of a covalent bond in the precursor ion to an electrostatic bond in the complex is often accompanied by rearrangement of the cation moiety $\mathrm{R^+}$, as revealed by the structures of the recovered alkenes. This communication reports the migratory aptitude of a fluorine relative to a methyl in the Wagner–Meerwein rearrangement schematically depicted in reaction 2. We have measured this using the electron bombardment flow (EBFlow) technique[2] to collect neutral products of reaction 1 where ROPh is 2-fluoro-2-methyl-1-phenoxypropane. Our results provide evidence for intramolecular fluorine transfer via a bridged fluoronium ion.

Experimental evidence for bridged fluoronium ions is surprisingly scant. Unlike the corresponding chloronium and bromonium ions,[3] whose stability in both gas phase and solution are well attested, neither fluoriranium (three-member ring) nor any larger cyclic ions have been unambiguously shown to exist (not even as transition states). In 1983 Ciommer and Schwarz reported experimental results consistent with the intermediacy of the simplest symmetrical case, ion **1**, in the gas phase.[4] Their isotopic scrambling data, though, could be equally well explained in terms of structure **2**, an ion–molecule complex between a symmetrically bridged vinyl cation (the most stable $\mathrm{C_2H_3^+}$ geometry[5]) and hydrogen fluoride. Since ion–molecule complexes between vinylic cations and hydrogen fluoride correspond to local minima on SCF potential energy surfaces,[6] such an option cannot be dismissed out of hand.

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[1] (a) Morton, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 1596–1602. (b) Hall, D. G.; Morton, T. H. *J. Am. Chem. Soc.* **1980**, *102*, 5686–5688. (c) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195–3243.

[2] Morton, T. H. In Techniques for the Study of Ion-Molecule Reactions. *Techniques of Chemistry XX*; Farrar, J. M., Saunders, W. H., Jr., Eds.; Wiley Interscience: New York, 1988; pp 119–164.

[3] (a) Olah, G. A. Halonium Ions; Wiley: New York, 1975. (b) Holmes, J. L.; Lossing, F. P.; McFarlane, R. A. *Int. J. Mass Spectrom. Ion Proc.* **1988**, *86*, 209–215.

[4] Ciommer, B.; Schwarz, H. *Z. Naturforsch.* **1983**, *38B*, 635–638.

[5] (a) Pople, J. A. *Chem. Phys. Lett.* **1987**, *137*, 10–12. (b) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1988**, *88*, 7405–7409. (c) Kanter, E. P.; Vager, Z.; Both, G.; Zajfman, D. *J. Chem. Phys.* **1986**, *85*, 7487–7488. (d) Oka, T. *Phil. Trans. R. Soc. London A* **1988**, *324*, 81–95.

[6] Stams, D. A.; Johri, K. K.; Morton, T. H. *J. Am. Chem. Soc.* **1988**, *110*, 699–706.

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