Diprotonated Sapphyrin: A Fluoride Selective Halide Anion Receptor

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Abstract: Prior solid-state structural evidence (Sessler, J. L.; Cyr, M. J.; Lynch, V.; McGhee, E.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 2810-2813) served to indicate that the diprotonated form of 3,8,12,13,17,22-hexaethyl-2,7,18,23-tetramethylsapphyrin ($[2\cdot2H]^{2+}$), as its mixed fluoride-hexafluorophosphate salt, $[1\cdot2H\cdot F]\cdot PF_6$, is capable of encapsulating fluoride anion within its ca. 5.5 Å diameter pentaaza macrocyclic core. The present report describes solution-phase studies related to these earlier solid-state ones. Optical titration studies, carried out in MeOH, reveal that fluoride anion is bound to $[1\cdot2H]^{2+}$ with an affinity constant, K_s, of ca. 1×10^5 M^{-1} whereas neither chloride nor bromide anion is complexed ($K_s \leq 10^2$ M^{-1} for both). In dichloromethane, a large but incomplete (i.e. biphasic) decrease in the fluorescence lifetimes was observed for the dihydrochloride (τ_f = 0.88 (93%) and 4.8 (7%) ns) and dihydrobromide (τ_f = 0.31 (78%) and 4.3 (22%) ns) salts of $[1\cdot2H]^{2+}$ under conditions where the fluorescence lifetime of the dihydrofluoride salt (τ_f = 5.0 ns) remained high. From the fractional amplitudes involved, association constants of $(1.8 \pm 0.4) \times 10^7$ and $(1.5 \pm 0.3) \times 10^6$ M^{-1} were derived respectively for the binding of Cl^- and Br^- to $[1\cdot2H]^{2+}$ in CH_2Cl_2; a lower bound for fluoride anion complexation, $K_s > 10^8$ M^{-1}, was also determined. In this same solvent, the fluoride salt of $[1\cdot2H]^{2+}$ also displayed both oxidation and reduction waves that were shifted to more negative values (by ca. 100 and 150 mV, respectively) as compared to those of the chloride and bromide salts. Also, in CD_2Cl_2, substantial upfield shifts and a significant concentration dependence on the observed position of the central pyrrolic NH signals are found for both the difluoride and mixed fluoride-hexafluorophosphate salts of $[1\cdot2H]^{2+}$ (e.g., for 1·2HF: δ(NH) $\approx$ −4.6, −5.8, −6.0 at 1 mM and −7.6, −8.6, −8.8 ppm at 30 mM) that are not seen in either the dihydrochloride or dihydrobromide salts (δ(NH) $\approx$ −4.2, −4.5, −4.8, and −4.6, −4.8, −5.1 ppm, respectively). Taken together, these data are consistent with a solution-state model in which a single fluoride anion may be complexed within the plane of the diprotonated sapphyrin core whereas both chloride and bromide anions would necessarily need be bound in an out-of-plane ion-pair-like fashion. Support for an extension of this model to the solid state was obtained from an X-ray structure of the dihydrochloride salt, 1·2HCl, which revealed that the two chloride counteranions are complexed above and below the diprotonated sapphyrin core within hydrogen bonding distance of the nearest pyrrolic nitrogen centers.

Introduction

In recent years there has been considerable effort devoted to the preparation and study of anion-selective complexing agents. Although a number of elegant artificial anion receptors are now known,[1] the number of systems capable of effecting fluoride anion selective recognition or transport remains quite limited.[2] Indeed, we are aware of only a few examples. These include the spherical anion cryptates of Lehn,[1d,2f] the fluoride anion complexes of iron(III) porphyrins reported by Kadish and co-workers,[2a,b] and the fluoride anion complexes of protonated macrocyclic polyamines studied by Suet et al.[2c] Recently, however, we found that the diprotonated form of 3,8,12,13,17,22-hexaethyl-2,7,18,23-tetramethylsapphyrin, $[1\cdot2H]^{2+}$, a large "expanded" congener of 2,3,7,8,12,13,17,18-octaethylporphyrin, $[2\cdot2H]^{2+}$ (Figure 1), binds fluoride anion in the solid state as its mixed PF_6^--F^- salt (Figure 2)[3] and acts as an effective carrier for the through-transport of fluoride anion in a model three-phase [aqueous 1]-[CH_2Cl_2]-[aqueous 2] membrane system.[4] Taken together, these results, which have no parallel in simple porphyrin chemistry, have led us to consider that the diprotonated form of sapphyrin could be considered as a new type of anion-specific binding agent. At present, however, little is known about the exact nature of the various anion-to-$[1\cdot2H]^{2+}$ interactions in solution. Here, we present the results of detailed optical and electrochemical studies carried out in both methanol and dichloromethane and show that the diprotonated form of 1 ($[1\cdot2H]^{2+}$) acts as a fluoride selective halide receptor in these two solvents. In addition, we report the solid-state X-ray structure of the dihydrochloride salt of sapphyrin 1, 1·2HCl.

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Experimental Section

Materials. The decaalkyl sapphyrin, 3,8,12,13,17,22-hexaethyl-2,7,18,23-tetramethylsapphyrin, 1, was prepared by using a modification[3] of the method of Bauer et al.[5] and converted to its dihydrofluoride (1·2HF), dihydrochloride (1·2HCl), and dihydrobromide (1·2HBr) salts by treatment with dilute solutions of the appropriate hydrohalous acid. Although the dihydrochloride and dihydrobromide salts of 1 (1·2HCl and 1·2HBr) routinely gave elemental analyses consistent with their proposed stoichiometric formulation, interestingly, and importantly, the corresponding combustion data were found to vary widely from batch to batch in material that in all cases was considered to be the pure dihydrofluoride salt. In fact, depending on the nature of the crystallization vessel (glass vs plastic) and the extent of subsequent drying, the N to F ratio, expected to be 5:2 for 1·2HF, was found to vary anywhere from 5:1 to 5:5. This variation in relative stoichiometry reflects the well-known tendency of HF, a weak acid, to self-oligomerize via narcissistic-type hydrogen bonds;

(1) For overviews of anion binding receptors, see: (a) Lindoy, L. F. *The Chemistry of Macrocyclic Ligands*; Cambridge University Press: Cambridge, 1989, Chapter 5. (b) Kimura, E. *Top. Cur. Chem.* **1985**, *128*, 113-141. (c) Graf, E.; Lehn, J.-M. *J. Am. Chem. Soc.* **1976**, *98*, 6403-6405. (d) Lehn, J.-M. *Acc. Chem. Res.* **1978**, *11*, 49-57. (e) Dietrich, B.; Guilhem, J.; Lehn, J.-M.; Pascard, C.; Sonveaux, E. *Helv. Chim. Acta* **1984**, *67*, 91-104.

(2) For specific examples of fluoride binding and/or transport, see: (a) Kadish, K. M.; Rhodes, R. K. *Inorg. Chem.* **1983**, *22*, 1090-1095. (b) Bottomley, L. A.; Kadish, K. M. *Inorg. Chem.* **1981**, *20*, 1348-1357. (c) Suet, E.; Handel, H. *Tetrahedron Lett.* **1984**, *25*, 645-648. (d) Jung, M. E.; Xia, H. *Tetrahedron Lett.* **1988**, *29*, 297-300. (e) Newcomb, M.; Blanda, T. *Tetrahedron Lett.* **1988**, *29*, 4261-4264. (f) Dietrich, B.; Lehn, J.-M.; Guilhem, J.; Pascard, C. *Tetrahedron Lett.* **1989**, *30*, 4125-4128.

(3) Sessler, J. L.; Cyr, M. J.; Lynch, V.; McGhee, E.; Ibers, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 2810-2813.

(4) Sessler, J. L.; Ford, D. A.; Cyr, M. J.; Furuta, H. *J. Chem. Soc., Chem. Commun.* **1991**, 1733-1735.

(5) Bauer, V. J.; Clive, D. L. J.; Dolphin, D.; Paine, J. B., III; Harris, F. L.; King, M. M.; Loder, J.; Wang, S. W. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6429-6436.

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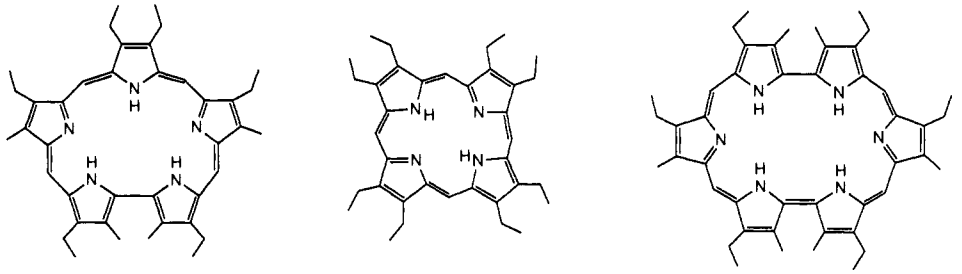


Figure 1. Schematic representation of the sapphyrin (**1**) and porphyrin (**2**) macrocycles used in this study. The diprotonated forms of sapphyrin are designated as $[1\cdot2H]^{2+}$, $[1\cdot2H\cdot F]^{+}$, 1·2HCl, etc. as appropriate; see text. Also shown is a schematic representation of rubyrin (**3**).

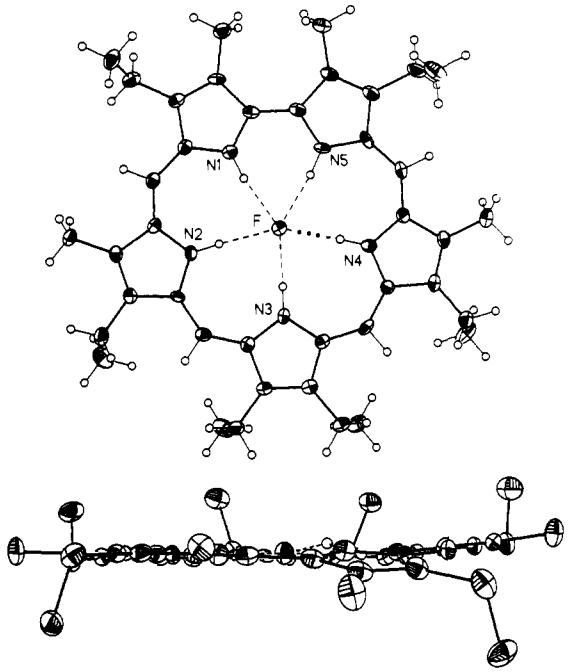


Figure 2. Two views of the molecular structure of the $[1\cdot2H\cdot F]^{+}$ cation showing the atom-labeling scheme. Non-hydrogen atoms are drawn with 50% ellipsoids; H atoms are drawn artificially small. Details of the core geometry are in ref 3.

it does not indicate that more than one F^- is binding to a "super protonated" form of sapphyrin. Fortunately, a reproducible preparation, obtained by washing a CH_2Cl_2 solution of **1** with 10% aqueous HF and drying under vacuum overnight at room temperature, could be obtained. It gave an N to F ratio of 5:5, which is consistent with 3 extra "spectator" molecules of HF being co-crystallized along with the desired (1·2HF) salt. Unless noted otherwise it was this material that was used throughout the present study. Moreover, since except for the quantitative binding constant determinations the presence of these extra molecules of HF was found to be largely inconsequential, for the sake of consistency, this solid material and solutions derived from it in all cases are referred to as being the simple dihydrofluoride salt of sapphyrin, 1·2HF. The analogous diprotonated salts of 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphyrin (H_2OEP), 2·2HF, 2·2HCl, and 2·2HBr, were also obtained from the free-base form by treatment with aqueous solutions of the appropriate hydrohalous acid. Tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) used for electrochemical studies was recrystallized from ethyl acetate. Tetra-*n*-butylammonium fluoride (TBAF) used for spectroscopic studies was purified by repeated dissolving (and then redissolving) the commercially available (Aldrich Chemical Co.) hydrated salt in toluene and pumping to dryness in vacuo; the corresponding tetra-*n*-butylammonium chloride and bromide salts (TBACl and TBABr, respectively) were purchased commercially and used without further purification. Solvents were spectroscopic grade and were used as received. Merck type 60 (230–400 mesh) silica gel was used for column chromatography. For $1\cdot5HF\cdot H_2O$: Anal. Calcd for $C_{40}H_{56}N_5F_5O$: C, 66.92; H, 7.86; N, 9.76; F, 13.23. Found: C, 67.20; H, 7.54; N, 9.56; F, 13.05. For 1·2HCl: Anal. Calcd for $C_{40}H_{51}N_5Cl_2$: C, 71.41; H, 7.64; N, 10.41; Cl, 10.54. Found: C, 71.65; H, 7.68; N, 10.41; Cl, 11.47. For $1\cdot2HBr\cdot H_2O$: Anal. Calcd for $C_{40}H_{53}N_5Br_2O$: C, 61.62; H, 6.85; N, 8.98; Br, 20.50. Found: C, 61.83; H, 6.73; N, 8.96; Br, 19.26.

General Methods. ^1H NMR spectra were recorded on a General Electric QE-300 (300 MHz) spectrometer. ^{19}F NMR spectra were recorded on a Nicolet NT-360 spectrometer. Elemental analyses were performed by Galbraith Laboratories. UV–visible spectra were taken on either a Hitachi U-3210 double-beam spectrophotometer or a Beckman Instruments DU-7 instrument. Fluorescence spectra were taken on a Perkin-Elmer Model LS-5 spectrofluorometer in methanol and dichloromethane using in all cases degassed solution and corrected for variations in instrumental response. Sample preparations were carried out in a darkened room. A Pine Instruments Co. Model RDE4 potentiostat/galvanostat was used for cyclic voltammetry measurements. Current–voltage curves were recorded on a Kipp & Zonen Model BD-90 recorder.

Binding Studies. The binding constant for fluoride anion complexation in methanol, K_s (K_s = [complex]/[diprotonated sapphyrin][X^-], where X^- represents the halogen anions; eq 1), was evaluated using a standard analysis[6] of the emission changes at 686 nm (Figure 5; vide infra) induced as a function of increasing TBAF concentration. From a plot (eq 2) of

$$\text{diprotonated sapphyrin} + X^- \rightleftarrows \text{complex} \qquad (1)$$

$(I_\infty - I_0)/(I - I_0)$ (where I_∞ represents the fluorescence intensity when diprotonated sapphyrin is completely converted to the bound form and I_0 is the extrapolated intensity at zero anion concentration)[7] vs $[F^-]^{-1}$ (see insert to Figure 5), a K_s value of $(9.6 \pm 2.0) \times 10^4$ M^{-1} for fluoride anion complexation at 296 K in MeOH was determined. The binding con-

$$(I_\infty - I_0)/(I - I_0) = 1 + 1/(K_s[F^-]) \qquad (2)$$

stants $K_s(Cl^-)$ and $K_s(Br^-)$, estimated as $\sim 10^2$ and $<10^2$, respectively, were obtained from the appropriate relative binding constants, $K_s(F^-)/K_s(X^-)$ (X = Cl or Br). These, in turn, were determined by adding increasing aliquots of TBACl or TBABr to a methanolic solution of the dihydrofluoride salt, 1·2HF.

Changes in absorption specra as a function of anion concentration were also used to calculate binding constants in MeOH. For the dihydrofluoride salt of **1**, a standard Benesi–Hildebrand analysis[8] of the absorption changes at λ_{max} 419 nm observed as a function of added fluoride anion gave a K_s value of $(2.8 \pm 0.5) \times 10^5$ M^{-1}. Similarly, monitoring the absorption changes at 421 nm as a function of increased chloride anion concentration gave a K_s value of $\sim 10^2$ M^{-1} for chloride anion complexation to diprotonated sapphyrin in MeOH. However, because of the small total change in absorptivity observed in these simple absorption-type titrations, the K_s values obtained from these studies are considered to be less accurate than those obtained from fluorescence analyses. In fact, a reliable K_s value for bromide anion binding could not be obtained using this method.

Electrochemical Measurements. Cyclic voltammetry measurements were performed under an argon atmosphere with a conventional three-electrode system. The working electrode was a platinum button (area ~ 0.03 cm^2), and a platinum wire was used as a counter electrode. An Ag/AgCl electrode was used as reference and was separated from the bulk solution by a fitted glass bridge which contained CH_2Cl_2 and the supporting electrolyte (0.1 M $TBAPF_6$). All potentials are recorded with respect to the ferrocene/ferrocenium (F_c/F_c^+) couple (=0.72 V vs Ag/AgCl) in CH_2Cl_2, 0.1 M $TBAPF_6$.

Singlet Excited-State Lifetimes. These were measured by time-correlated single-photon counting using a mode-locked, synchronously pumped, cavity-dumped dye laser (λ = 590 nm; instrument response

(6) Takla, P. G.; Schulman, S. G.; Perrin, J. H. *J. Pharm. Biomed. Anal.* **1985**, *3*, 41–50.

(7) The initial value, I_0, was approximated from an iterative linearization of eq 2.

(8) Benesi, H.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.

function fwhm 60 ps) as the excitation source.[9] Fluorescence was isolated from scattered laser light using a high radiance monochromator and attenuated before being detected with a Hamamatsu fast-response microchannel plate phototube. Data analysis was made by nonlinear minimization iterative procedures after deconvolution of the instrument response.

X-ray Structural Analysis. A single crystal of **1**·2HCl was obtained by vapor diffusion of diethyl ether into a $CHCl_3$ solution of **1**·2HCl. The data crystal was a dark blue prism of approximate dimensions 0.2 × 0.3 × 0.3 mm. Data were collected at room temperature on a Nicolet P3 diffractometer using a graphite monochromator and Mo Kα radiation (λ = 0.7107 Å). Details of the crystal data are listed in Table I. The lattice parameters were obtained from least-squares refinement of 39 reflections with $14.2 < 2\theta < 19.2°$. A total of 13 682 reflections were collected using the ω scan technique, of which 6583 were unique. R for averaging the symmetry equivalent reflections was 0.048. The data collection range was from 4.0 to 50.0° in 2θ with a 1.5° ω scan at 5–10°/min (h = −14→14, k = 0→19, l = −23→23). Three reflections (−1,5,−2; 4,2,−4; −2,−2,6) were remeasured every 97 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of the check reflections was used to scale the data. The scaling factor ranged from 0.997 to 1.05. The data were also corrected for Lp effects but not for absorption. No significant secondary extinction was observed. Reflections having $F_o < 4(\sigma(F_o))$ were considered unobserved (3672 reflections). The structure was solved by direct methods and refined by full-matrix least-squares procedures with anisotropic thermal parameters for the non-hydrogen atoms.[10] The hydrogen atoms were calculated in ideal positions with U_{iso} fixed at $1.2U_{eq}$ of the relevant atom. A total of 424 parameters were refined. The function, $\sum w(|F_o| - |F_c|)^2$, was minimized, where $w = 1/(\sigma(F_o))^2$ and $\sigma(F_o) = 0.5kI^{-1/2}[(\sigma(I))^2 + (0.02I)^2]^{1/2}$. The intensity, I, is given by $(I_{peak} - I_{background}) \times$ (scan rate), 0.02 is a factor to downweight intense reflections and to account for instrument instability, and k is the correction due to Lp effects and decay. $\sigma(I)$ was estimated from counting statistics; $\sigma(I) = [(I_{peak} + I_{background})^{1/2}$(scan rate)]. Final R = 0.0696 for 2911 reflections, R_w = 0.0656 (R for all reflections = 0.159, R_w for all reflections = 0.0889), and the goodness of fit is 1.280. The maximum |shift/esd| < 0.1 in the final refinement cycle and the minimum and maximum peaks in the final difference electron density map were −0.40 and 0.40 e$^-$/Å^3, respectively. The scattering factors for the non-H atoms were taken from Cromer and Mann,[11] with anomalous-dispersion corrections taken from Cromer and Liberman,[12] while scattering factors for the H atoms were obtained from Stewart, Davidson, and Simpson.[13] The linear absorption coefficient was obtained from values found in the *International Tables for X-ray Crystallography*.[14] Other computer programs are listed in ref 11 of Gadol and Davis.[15]

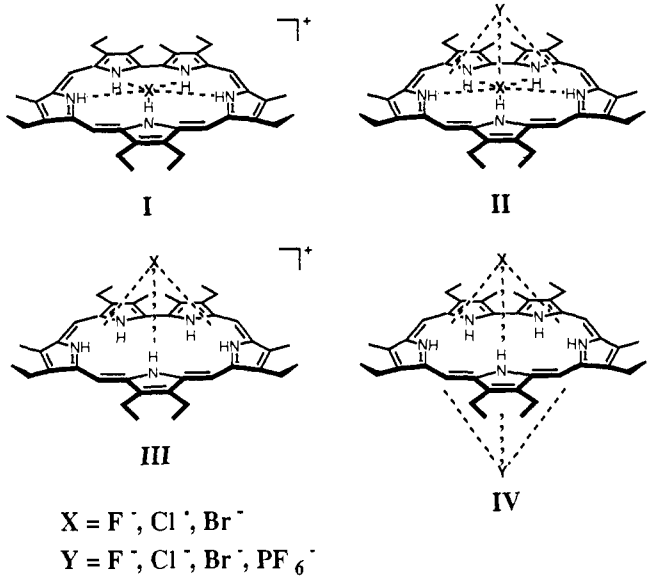
Results and Discussion

Nature of the Problem. Earlier, we reported the single-crystal X-ray analysis of the mixed F^-–PF_6^- salt of the diprotonated form of sapphyrin (**1**·HF·HPF_6).[3] As seen in Figure 2, the fluoride anion is held by a pentagonal array of N—H···F hydrogen bonds within the ca. 5.5 Å diameter core of the fully protonated macrocycle. As outlined in the introduction, this finding led us to consider that the diprotonated form of this "expanded porphyrin" could act as a fluoride anion selective halide receptor both in solution and in the solid state. The present study was undertaken as a test of this hypothesis.

As we define it, the problem is 3-fold: First, we considered it necessary to determine whether the diprotonated form of sapphyrin displays a higher relative affinity for fluoride anion compared to other halide anions in solution. Second, we felt it desirable to carry out an X-ray diffraction analysis of a diprotonated sapphyrin complex containing some halide anion larger than fluoride to determine whether the in-plane fluoride anion complexation observed for **1**·HF·HPF_6 is reproduced in the case of the corresponding larger halide-containing complexes. Finally, to the extent that such a determination could be made, we sought to define the nature of the [anion]-to-[diprotonated sapphyrin] complex(es) which exist in solution.

Table I. Crystallographic Data for **1**·2HCl

chemical formula	$C_{40}H_{51}N_5Cl_2$	crystal system	monoclinic
fw	672.78	space group	$P2_1/n$ (No. 14)
a, Å	12.126 (3)		
b, Å	16.089 (5)	T, °C	298
c, Å	19.424 (5)	ρ, g cm^{-3}	1.20
β, deg	101.01 (2)	μ (Mo Kα, λ = 0.7107 Å), cm^{-1}	2.066
V, Å^3	3720 (2)	R	0.0696
Z	4	R_w	0.0656
F(000)	1440	goodness-of-fit	1.280



Structures I–IV represent potential modes for possible [anion]-to-[diprotonated sapphyrin] interaction both in solution and in the solid state. Clearly these represent limiting structures. Moreover, they are only schematic depictions (i.e. the dotted lines are not meant to imply specific bonds but just generalized association). Nonetheless, as outlined above, a major goal of this study was to establish to what extent and under what conditions the various dihydrohalide salts of sapphyrin **1** could be represented by one or more of these limiting structures. Therefore, we have carried out an X-ray diffraction analysis of the dihydrochloride salt of sapphyrin, **1**·2HCl, in the crystalline state and have investigated the electronic absorption and emission properties of the dihydrofluoride, dihydrochloride, and dihydrobromide salts of **1** in MeOH solution and the ^{1}H NMR, cyclic voltammogram, electronic absorption, and fluorescence emission properties of these same salts in CH_2Cl_2.[16] Each of these studies is now discussed in turn.

X-ray Structure of Sapphyrin Dihydrochloride (1·2HCl). The X-ray structure of the dihydrochloride salt of sapphyrin, **1**·2HCl, is shown in Figure 3. The structure of this complex is very different from that of the mixed hydrofluoride–hydrohexafluorophosphate complex, **1**·HF·HPF_6, displayed in Figure 2. Whereas in the latter, the fluoride anion is held within the plane of the sapphyrin by the five NH hydrogen bonding donor groups, in the case of the dihydrochloride salt, the two chloride anions are found to be complexed in a near symmetric fashion above and below the sapphyrin plane. Thus, to a first approximation the structure of **1**·2HCl can be considered as being that of a gener-

(9) O'Connor, D. V.; Phillips, D. *Time Correlated Single Photon Counting*; Academic Press: London, 1984.
(10) SHELXTL-*PLUS* (1989): Siemens Analytical X-ray Instruments, Inc., Madison, WI.
(11) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321–324.
(12) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.
(13) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Phys. Chem.* **1965**, *42*, 3175–3187.
(14) *International Tables for X-ray Crystallography*; Birmingham: Kynoch Press, 1974; Vol. IV, p 55.
(15) Gadol, S. M.; Davis, R. E. *Organometallics* **1982**, *1*, 1607–1613.
(16) The hydroiodide complex proved difficult to prepare in pure form. Therefore, it has been omitted from the present study. Redox reactions, which occur during preparation, apparently produce small amounts of I_2, which we have found difficult to remove.

Table II. UV/Visible Absorption Data and Redox Potentials ($E_{1/2}$, V vs F_c/F_c^+) for **1**·2HX (X = F, Cl, and Br)

1·2HX X =	absorption, λ_{max}, nm (log ϵ) in CH_2Cl_2			in CH_3OH		$E_{1/2}$,[b] V vs F_c/F_c^+ 1st oxd.	1st red.	2nd red.	ΔE_{red}[c]
F	446 (5.81)	572 (3.33)	619 (4.17)	443 (5.79)	616 (4.15)	+0.68	−1.20	−1.46	260
		670 (4.19)	676 (4.12)[a]		668 (4.27)				
Cl	456 (5.73)	576 (3.76)	624 (4.19)	443 (5.81)	616 (4.23)	+0.76	−1.05	−1.21	160
		675 (4.29)	z686 (4.26)		668 (4.31)				
Br	458 (5.72)	578 (3.43)	624 (4.18)	443 (5.78)	616 (4.23)	+0.80	−1.04	−1.20	160
		678 (4.30)	689 (4.24)[a]		668 (4.31)				

[a] Shoulder. [b] 0.1 M $^nBu_4NPF_6$ in CH_2Cl_2, scan rate = 100 mV/s^{-1}. [c] $\Delta E = E_{1/2}$(1st red.) − $E_{1/2}$(2nd red.) (mV).

alized type IV, whereas the fluoride complex **1**·HF·HPF_6 would be a type I structure.

These structural results are not unexpected and probably just reflect the relative size of fluoride and chloride anion (atomic radii 1.19 and 1.67 Å,[17] respectively) and the rather inflexible nature of the ca. 5.5 Å sapphyrin cavity. What is interesting, however, is that in both complexes well-defined NH-to-halide hydrogen bonds appear to be playing a dominant role in defining the specifics of the observed solid-state structure. In the case of **1**·HF·HPF_6 these bonds are nearly equal at an N-to-F distance of 2.7 Å, in accord with the proposed NH–F hydrogen bonding interactions. On the other hand, in **1**·2HCl, the N-to-Cl distances range from 3.189 (5) to 3.413 (5) Å for Cl1 and 3.128 (5) to 3.631 (6) Å for Cl2 with Cl1 being closer to N3, N4, and N5 (3.200 (3) Å av) and Cl2 being closer to N1 and N2 (3.157 (4) Å av). This has the affect of placing the chloride anions ca. 1.8 Å above and below the macrocycle plane. It also allows a slight buckling of the sapphyrin macrocycle in a way that is without correspondence in the case of **1**·HF·HPF_6.

In the context of the above discussion, it is interesting to compare the X-ray structure of **1**·2HCl with those of two other structurally characterized pyrrole-containing macrocyclic systems, namely tetrapyridylporphyrin hexahydrochloride (TPyP·6HCl)[18] and rubyrin dihydrochloride (Rub·2HCl),[19] a diprotonated salt of the hexapyrrolic expanded porphyrin system, **3**. In this comparison, several features are of note. First, the observed closest N-to-Cl distances are found to be nearly equal (at ca. 3.1–3.2 Å) for all three hydrochloride salts, reflecting, presumably, the strong hydrogen bonding interactions pertaining in all three cases. Second, although the structure of TPyP·6HCl is markedly distorted away from planarity as the result of strong steric and electrostatic interactions (both adjacent and transverse) between inner NH moieties, the two expanded porphyrin systems **1**·2HCl and **3**·2HCl are nearly planar (to within 0.5 Å). Third, the chloride counteranion is found to be ca. 2.6, 1.8, and 1.6 Å above (and below) the mean macrocycle planes in the case of TPyP·6HCl, **1**·2HCl, and **3**·2HCl, respectively. Finally, it is found that the position of the two chloride anions is shifted from the center axes (of the macrocycle planes) in both **1**·2HCl and **3**·2HCl (0.27 (av) and 0.87 Å, respectively), a phenomenon not seen in the simple porphyrin case.

Taken together, the above results are consistent with a model in which, for all of these structures, a balance is struck between maximizing the extent of the NH-to-Cl hydrogen bonds and minimizing the effect of unfavorable steric and electronic interactions. In particular it is suggested that a larger cavity size allows for a flattening of the overall structure both by the release of untoward adjacent in-plane NH-to-NH steric hindrance and the minimization of various electrostatic repulsions including those involving through-plane Cl^--to-Cl^- and transverse, in-plane NH^+-to-NH^+ interactions.

Absorption and Emission Studies in Methanol. In previous work,[20] it was found that the dihydrochloride salt of sapphyrin, **1**·2HCl, was prone to dimerize in polar media with a specific dimerization constant of (1.2 ± 0.3) × 10^4 M^{-1} being determined in MeOH.[20a] Thus, we were forced to work at very low concentrations. In fact, unless otherwise indicated, a concentration of 2.6 × 10^{-6} M was used for all studies. Under these conditions, dimerization is negligible (as confirmed by linear Beer's law plots in the 1.0 × 10^{-6} to 5.0 × 10^{-6} M regime).[21] As a consequence of working at low concentration, studies in methanol were limited to simple absorption and fluorescence emission analyses.

Figure 4 shows the absorption spectra of the dihydrofluoride, dihydrochloride, and dihydrobromide salts of sapphyrin **1** recorded in methanol. Each spectrum exhibits an intense Soret-like band at 443 nm and two weaker Q-type bands at 616 and 668 nm (Figure 4 and Table II). Interestingly, these spectra are similar to that of the crystallographically characterized complex **1**·HF·HPF_6 in methanol[3] and the dihydrofluoride salt, **1**·2HF, in CH_2Cl_2 but quite different from those observed for **1**·2HCl and **1**·2HBr in CH_2Cl_2 (vide infra).[22]

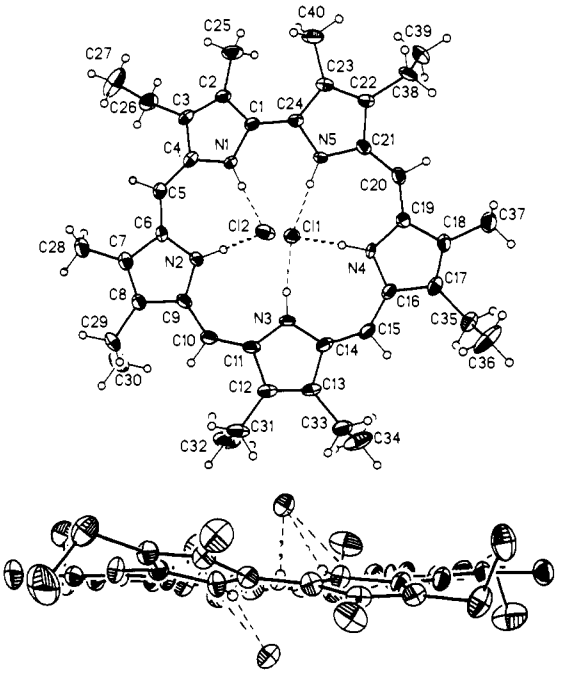


Figure 3. Two views of the molecular structure of complex **1**·2HCl with one view approximately perpendicular to the plane through the N atoms showing the atom labeling scheme and the second view illustrating the nearly planar nature of the macrocycle. Thermal ellipsoids are scaled to 30% probability level; H atoms are drawn to an arbitrary size. N···Cl contacts shorter than the sum of their van der Waals radii (3.3 Å) are indicated by dashed lines from Cl^- to H. The relevant Cl···N contacts (Å) for Cl1 are N1 3.413 (5), N2 3.383 (6), N3 3.212 (5), N4 3.198 (5), N5 3.189 (5) and those for Cl2 are N1 3.128 (5), N2 3.186 (5), N3 3.339 (5), N4 3.631 (6), N5 3.400 (5). Cl1 lies 1.773 (2) Å above the plane of the five N atoms while Cl2 is 1.877 (2) Å below it. Cl1 is 0.24 Å and Cl2 is 0.29 Å from a line perpendicular to this plane and passing through the centroid of the five N atoms. The Cl···Cl separation is 3.678 (3) Å.

(17) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767.
(18) Stone, A.; Fleischer, E. B. *J. Am. Chem. Soc.* **1968**, *90*, 2735–2748.
(19) Sessler, J. L.; Morishima, T.; Lynch, V. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 977–980.
(20) (a) Maiya, B. G.; Cyr, M.; Harriman, A.; Sessler, J. L. *J. Phys. Chem.* **1990**, *94*, 3597–3601. (b) Regev, A.; Michaeli, S.; Levanon, H.; Cyr, M.; Sessler, J. L. *J. Phys. Chem.* **1991**, *95*, 9121–9129.

(21) Calculated to be <3% for the dichloride salt. See ref 20a.

Table III. Luminescence Properties of Excited States of 1·2HX (X = F, Cl, Br) in CH_2Cl_2 and CH_3OH at Room Temperature

	emission					
	in CH_2Cl_2			in CH_3OH		
1·2HX X =	λ_{max},[a] nm	Φ^1_{rel}[b]	τ_f,[c] ns	λ_{max},[d] nm	Φ^1_{rel}[b]	τ_f,[c] ns
F	683	1.0	5.0	686	1.0	4.7
Cl	685	0.17	0.88 (93), 4.8 (7)[e]	682	0.85	4.3
Br	695	0.05	0.31 (78), 4.3 (22)[e]	682	0.85	4.3

[a] The excitation wavelengths are 446, 456, and 458 nm for 1·2HF, 1·2HCl, and 1·2HBr, respectively. [b] Relative quantum yield of the singlet state; estimated error ≤10%. [c] Lifetime of the singlet state; estimated error ≤5%. [d] The excitation wavelength is 443 nm for all samples. [e] Two components were observed; values in parentheses are their distribution percentages.

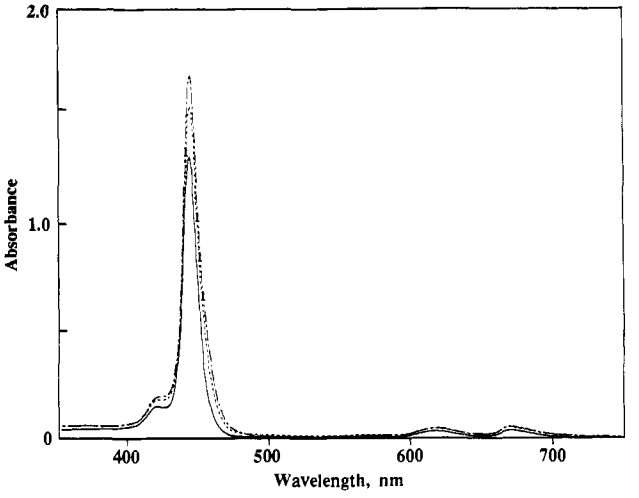


Figure 4. Absorption spectra for the diprotonated form of sapphyrin recorded in CH_3OH: (—) for the dihydrofluoride salt of **1**; (- - -) for the dihydrochloride salt of **1**; and (- · -) for the corresponding dihydrobromide salt. The concentration of $[1·2H]^{2+}$ is roughly 20% lower for the dihydrofluoride salt than in the case of the dihydrochloride and dihydrobromide salts.

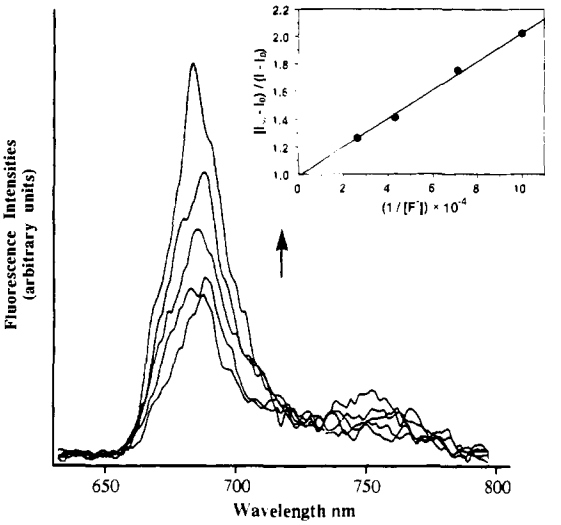
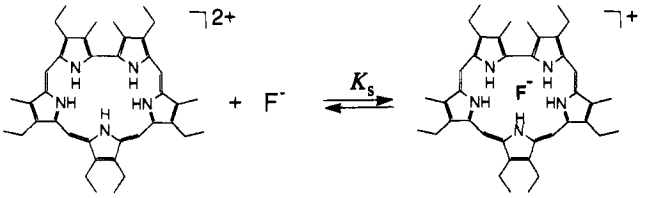


Figure 5. Emission enhancements for the dihydrofluoride salt of **1** as a 2.6×10^{-6} M solution in MeOH as a function of increased fluoride anion concentration. Tetra-*n*-butylammonium fluoride (TBAF) was used as a fluoride source; $[F^-] = 9.3 \times 10^{-6}$, 1.4×10^{-5}, 2.3×10^{-5}, 3.9×10^{-5}, and 2.4×10^{-4} M, from the bottom. The insert shows a plot to eq 2 and gives a K_s value of $(9.6 \pm 2.0) \times 10^4$ M^{-1} for fluoride anion complexation at 296 K; see text.

Addition of increasing aliquots of tetra-*n*-butylammonium fluoride (TBAF) to a solution of the dihydrofluoride salt in MeOH led to an increase in the observed absorption shoulder at 419 nm and a slight blue shift of the Soret band to 441 nm. Although the total change in absorptivity was small (even at 419 nm), the data could be fit to a 1:1 equilibrium process using a standard Benesi-Hildebrand treatment (cf. experimental).[8] This gave an approximate binding constant of $(2.8 \pm 0.5) \times 10^5$ M^{-1} for fluoride binding in MeOH at 296 K. Similar titrations were carried out by adding increasing quantities of tetra-*n*-butylammonium chloride (TBACl) or tetra-*n*-butylammonium bromide (TBABr) to the dihydrochloride or dihydrobromide salts of **1**. A K_s value of ca. 10^2 M^{-1} was estimated for the complexation of Cl^- with $[1·2H]^{2+}$ at 296 K in MeOH, but the stability constant with Br^- could not be determined in this way.

More reliable values of the relative binding constants were obtained from fluorescence emission studies. Figure 5 shows the fluorescence emission spectrum of the dihydrofluoride salt of **1** in MeOH at 296 K and the result that adding increasing equivalents of TBAF has upon this spectrum. Although some noise is observed in the various spectral traces (presumably a consequence of the low concentration used), clear and discernable changes are observed as a function of total anion concentration. Now, a standard analysis[6] fit to a 1:1 binding process could be made by plotting changes in emission intensity relative to fluoride anion concentration. This gave a value of K_s of $(9.6 \pm 2.0) \times 10^4$ M^{-1} at 296 K, corresponding to a stabilization energy of 28.2 kJ mol^{-1}.

Scheme I



By adding excess chloride or bromide anion (as the tetra-*n*-butylammonium salts) to this same starting fluoride solution and by using the ratio of fluorescence intensity for the pure dihydrohalide salts (Table III), K_s values of ca. 10^2 M^{-1} ($\Delta G \sim -11.3$ kJ mol^{-1}) and $<10^2$ M^{-1} could be derived for chloride and bromide binding to $[1·2H]^{2+}$, respectively, at 296 K in this solvent.[23]

The observed F^-/Cl^- or Br^- selectivity is extremely high (more than 1000-fold!) and is completely unexpected on the basis of a

(22) On the basis of the measured pK'_a values for the dihydrochloride salt of **1**, these observed spectral differences are not ascribed to the differences in degrees of protonation of the sapphyrin core (i.e. monoprotonated vs diprotonated entities in MeOH or dichloromethane) but to more subtle features associated with the nature of the interaction between the diprotonated sapphyrin dication and the halide anion counteranions. In 68.1:31.9 MeOH/H_2O the deprotonation constants of the dihydrochloride and the monohydrochloride salt of **1** (pK'_1 and pK'_2) were found to be ca. 6.3 and 8.4, respectively. In pure methanol, therefore, where the proton affinities of the sapphyrin core might be expected to be higher than in this mixed solvent, the concentration of monoprotonated species would be expected to be less than 10% at the 2.6×10^{-6} M concentration studied. For measurements of pK'_a values in alcohol–water solvent systems, see: Bates, R. G.; Paabo, M.; Robinson, R. A. *J. Phys. Chem.* **1963**, *67*, 1833–1838.

(23) At very high Cl^- concentrations ($>10^{-2}$ M) a new emission at 715 nm, characteristic of photodimers, appeared with the disappearance of the emission band at 683 nm.

normal Hofmeister progression.[24] The simplest explanation is to attribute this high relative selectivity to the fact that fluoride anion (ionic radius ca. 1.19 Å[17]) can be accommodated within the ca. 5.5 Å diameter diprotonated inner sapphyrin cavity whereas its two large congeners, chloride and bromide (ionic radii: 1.67 and 1.82 Å, respectively[17]), can not. Thus, the K_s equilibria values measured above are consistent with a binding model that permits the formation of a 1:1 centrally encapsulated complex of general structure I in the case of fluoride *only* (Scheme I) and requires the formation of out-of-plane ion-paired complexes of generalized structure III and/or IV in the case of both chloride and bromide binding. Although not a proof of structure in solution (other explanations for the relative K_s values could be envisioned), these binding studies do confirm that, relative to either chloride or bromide, the diprotonated form of sapphyrin is a highly selective receptor for fluoride anion in dilute MeOH solution.

The measured fluorescence properties in MeOH further support the proposed encapsulation of fluoride. In very dilute MeOH solution ($[\mathbf{1}\cdot 2H]^{2+} \ll 2.6 \times 10^{-6}$ M) the fluorescence (relative) quantum yields and lifetimes measured for the various salts are identical within experimental limitations. Under these conditions, the complexes are fully dissociated and the emitting species, in each case, is the free diprotonated sapphyrin moiety. Increasing the concentration of the counteranion (or raising the concentration of the salt) induces complexation and, for the dihydrofluoride salt, this is accompanied by an increase in both fluorescence yield and lifetime (cf. Figure 5 and Table III).[25] This increase is best explained by central fluoride encapsulation. It is well-known that the central N–H bonds in free-base tetrapyrrolic pigments function as very effective vibrational energy sinks for dissipating the photonic energy via internal conversion.[26] The presence of a cavity-bound fluoride ion should, therefore, decrease the rate of nonradiative deactivation of the excited singlet state by eliminating this important decay mode. The proposed in-cavity fluoride anion binding thus accounts for the increase in fluorescence in a way that other, alternative binding modes would not.

Studies in Dichloromethane. In an effort to facilitate the use of other experimental methods, further studies were carried out in dichloromethane. In this less polar solvent, the dihydrochloride salt of sapphyrin is known to be monomeric and to obey Beer's law over a wide concentration range (0–10^{-4} M).[20a] Figure 6 shows the upfield, internal pyrrolic region of the ^{1}H NMR spectra of the dihydrobromide, dihydrochloride, and dihydrofluoride salts of **1** recorded at ca. 10^{-3} M in CD_2Cl_2 as well as the spectrum of the structurally characterized mixed hydrofluoride–hydrohexafluorophosphate salt recorded under identical experimental conditions. It is clear that the nature of the counteranion has a profound effect on this region of the ^{1}H NMR spectrum. For instance, in the case of the dihydrochloride and dihydrobromide salts, the spectra show three singlets upfield of tetramethylsilane, which are readily assigned to the pyrrolic NH protons. The 2:1:2 resonance pattern indicates the presence of three types of nonequivalent central protons which undergo slow interchange on the NMR time-scale.[27] In contrast, three characteristic doublets with a 1:2:2 resonance pattern were observed in the case of **1**·HF·HPF_6.

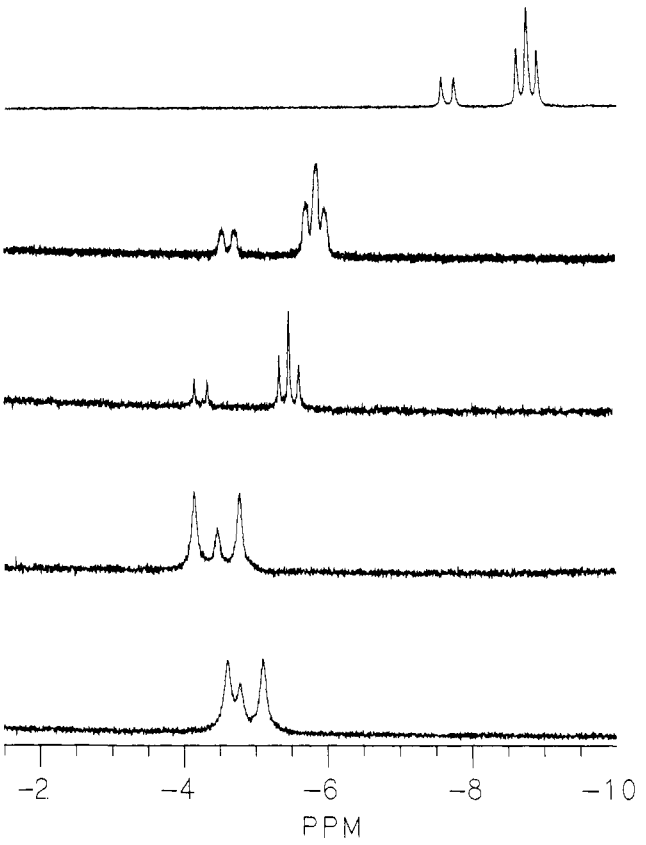


Figure 6. Portions of ^{1}H NMR spectra of, from the bottom up, **1**·2HBr, **1**·2HCl, **1**·HF·HPF_6, and **1**·2HF recorded at 1 mM CD_2Cl_2. Also shown as the top trace is the ^{1}H NMR spectrum of **1**·2HF recorded at 30 mM CD_2Cl_2. The signals observed between −2 and −10 ppm are assigned to pyrrolic N–H protons.

These signals were found at higher field than in the corresponding hydrochloride and dihydrobromide salts and, in addition, they showed clear splitting behavior assignable to ^{1}H–^{19}F coupling (J = 40–50 Hz).[28] Similar coupling patterns with considerable upfield shifts were observed in the case of the dihydrofluoride salt of **1**. In both **1**·HF·HPF_6 and **1**·2HF cases, however, the exact position of the pyrrolic N–H proton signal was observed to change substantially as a function of specific sample concentration in CD_2Cl_2 (e.g., for **1**·2HF: δ(NH) ≈ −4.6, −5.8, −6.0 at 1 mM and −7.6, −8.6, −8.8 ppm at 30 mM; cf. Figure 6), reflecting the formation of dimers and/or aggregates at higher concentrations of these salts. Such concentration-dependent shifts were not observed for **1**·2HCl and **1**·2HBr in this solvent.

Taken together the above results are consistent with a picture wherein tight ion pairing pertains between $[\mathbf{1}\cdot 2H]^+$ and Br^- and Cl^- but in which no direct counteranion encapsulation occurs within the sapphyrin core (cf. generalized structure IV and the solid-state structure of Figure 3).[27] On the other hand, the ^{1}H NMR spectrum of the mixed hydrofluoride–hydrohexafluorophosphate salt of **1** is consistent with an encapsulated fluoride anion and a solution-phase structure, of generalized type I (the relatively large upfield shifts being rationalized in terms of the increased charge neutralization provided by central anion encapsulation as opposed to simple "external" ion pairing). The qualitative correspondence between the spectra of this structurally characterized mixed HF–HPF_6 species and that of the dihydrofluoride salt leads

(24) Such a series is based on the relationship between the size of the anion and the entropy of binding (see: Fridovich, I. *J. Biol. Chem.* **1963**, *238*, 592–598).

(25) At 2.6×10^{-6} M, approximately 17% of the compound will be present as the fluoride-bound form but neither chloride nor bromide will be bound. Diluting the HF salt solution with methanol reduces the amount of bound fluoride and lowers both fluorescence yield (to a limiting value of 0.87 relative the 1.0 value cited for **1**·2HF in Table III) and lifetime (to a limit of 4.4 ns). As mentioned in the text, adding excess fluoride increases the yield (see Figure 5) and lifetime (to 5.5 ns). Most likely, therefore, the lifetime at 2.6×10^{-6} M is really a mixture of 2 lifetimes (4.4 and 5.5 ns) that are too similar to be resolved properly.

(26) (a) Engelman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145–164. (b) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 3, Chapter 1. (c) Kurabayashi, Y.; Kikuchi, K.; Kokubun, H.; Kaizu, Y.; Kobayashi, H. *J. Phys. Chem.* **1984**, *8*, 1308–1310.

(27) The somewhat broadened peaks observed with both the dihydrochloride and dihydrobromide salts suggest a mixture of species of structural types III and IV.

(28) ^{19}F NMR studies were carried out in an attempt both to analyze further the nature of this H-to-F coupling and to define more precisely the nature of the bound fluoride anion complex formed in solution. However, in contrast to the proton NMR analyses, these studies proved rather uninformative. In CD_2Cl_2 solution the chemical shift of free fluoride anion was observed at 153.5 ppm whereas that of bound fluoride anion was 153.4 ppm. In neither case could any detectable H-to-F coupling be observed; the width of the signals was just too large.

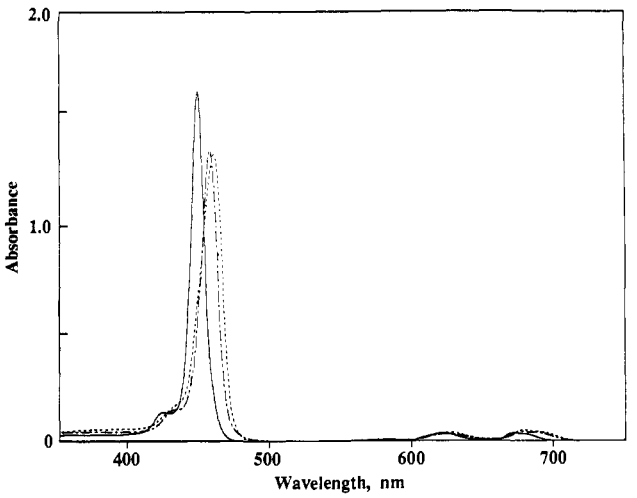


Figure 7. Absorption spectra for the diprotonated form of sapphyrin recorded in CH_2Cl_2: (—) for the dihydrofluoride salt of **1**; (- - -) for the dihydrochloride salt of **1**; and, (- - -) for the corresponding dihydrobromide salt. In all cases the concentration of $[1\cdot2H]^{2+} = 2.6 \times 10^{-6}$ M.

us to suggest that this latter material also contains a fluoride anion centrally encapsulated within the sapphyrin cavity. However, further ion-pairing interactions, which are modeled by generalized structure II, could be important in this material at higher concentrations.

Figure 7 shows the absorbance spectra for the dihydrofluoride, dihydrochloride, and dihydrobromide salts of **1** recorded at 2.6×10^{-6} M CH_2Cl_2. In marked contrast to the corresponding results obtained in MeOH, now a clear and discernable anion dependence is observed. As compared to the chloride- and bromide-derived materials, the spectrum of the dihydrofluoride salt displays a sharpened Soret-like maximum that is blue-shifted by ca. 10 nm. In addition, the nature and position of this peak (and the others in the spectrum) are the same as for the structurally characterized mixed $HF-HPF_6$ salt.

Again, these observations can be rationalized in terms of a model wherein extensive ion pairing exists for the dihydrochloride and dihydrobromide salts and central monofluoride anion encapsulation occurs for the fluoride anion-containing salts. Unfortunately, attempts to obtain quantitative binding data in this solvent using UV/vis methods proved unsuccessful. Slow rates of apparent anion exchange interfered with with attempts to set up well-defined equilibria and precluded the determination of any meaningful K_s values.[29] Therefore, more detailed photophysical analyses of the excited singlet state were carried out.

Fluorescence spectra recorded for the dihydrofluoride, dihydrochloride, and dihydrobromide salts of **1** in degassed CH_2Cl_2 solution are displayed in Figure 8a. The spectra differ significantly and, unlike methanol solution, it is clear that the nature of the emitting species differs in each case. This conclusion is strengthened by the observation that fluorescence yields and lifetimes are markedly dependent on the type of counteranion employed (Table III). Under the same conditions, however, there was no corresponding anion dependence for the photophysical properties of the OEP-derived salts (**2**·2HX; X = F, Cl, Br) (Figure 8b). This behavior is consistent with pronounced anion complexation occurring in the sapphyrin series but not in the corresponding porphyrin salts.

Relative to the dihydrofluoride sapphyrin salt (**1**·2HF), fluorescence from the dihydrochloride and dihydrobromide salts is extensively quenched. Quenching is attributed to the internal heavy-atom effect in which the halide counteranion promotes nonradiative deactivation of the excited singlet state via a spin–orbit coupling mechanism.[30] Indeed, ns-laser flash photolysis studies indicate that the efficiency for intersystem-crossing to the triplet manifold increases in the order **1**·2HF < **1**·2HCl < **1**·2HBr, exactly as predicted for a spin–orbital coupling mechanism.[31] This mechanism operates only over short distances. Therefore, the counteranion must be closely bound to the sapphyrin chromophore. Most likely, the HCl and HBr salts exist as electrostatically-bound ion-pairs for which, according to the Fuoss equation,[32] the degree of dissociation will decrease with decreasing dielectric constant of the solvent.

The time-resolved fluorescence studies made with these latter salts (viz. **1**·2HCl and **1**·2HBr) indicate the presence of two components, one possessing a very short lifetime and the second having a lifetime similar to that assigned to uncomplexed diprotonated sapphyrin in methanol solution (Table III). Thus, the short lifetime is attributed to the ion-pair and the long lifetime to the dissociated species in CH_2Cl_2 solution. From the fractional amplitudes of these two components (Table III), the association constants, K_s, for ion-pairs formed with HCl and HBr are calculated to be $(1.8 \pm 0.4) \times 10^7$ and $(1.5 \pm 0.3) \times 10^6$ M^{-1}, respectively.[33] Upon inserting these derived values into the Fuoss equation, we conclude that the ion-pairs should be completely dissociated in methanol solution under the conditions used for the fluorescence measurements.[34]

For the corresponding dihydrofluoride salt (**1**·2HF) in CH_2Cl_2 solution, the fluorescence decay profile could be analyzed satisfactorily in terms of a single exponential fit. The derived lifetime ($\tau_f = 5.0$ ns), which is similar to that found in methanol solution ($\tau_f = 4.7$ ns) and to that recorded for free-base sapphyrin in CH_2Cl_2 solution ($\tau_f = 4.7$ ns), shows minimal quenching of the sapphyrin fluorescence by the fluoride counteranion. The observation of a single component, taken together with the other spectroscopic data recorded for the dihydrofluoride sapphyrin salt in this solvent, is consistent with $K_s > 10^8$ M^{-1}. The absence of any significant quenching effect[35] is thus consistent with the fluoride anion being encapsulated within the central sapphyrin cavity, as outlined above. In particular, the expected quenching due to spin–orbital coupling via the fluoride anion is offset by elimination of the central N–H bond as a vibrational energy sink.

The unique fluoride complex formation detailed above also affects the redox potential of the diprotonated sapphyrin system. Cyclic voltammograms for the difluoride, dichloride, and dibromide salts of **1** recorded in CH_2Cl_2 containing 0.1 M $TBAPF_6$ at 24 ± 1 °C are given in Figure 9. All compounds exhibit two quasireversible reduction and one quasireversible oxidation couples as shown in Table II. The first and second reduction couples of

(29) The fluoride anion binding constant previously reported for $CHCl_3$ solution should be discounted (see: Sessler, J. L.; Cyr, M. J.; Burrell, A. K. *Synlett* **1991**, 127–134). The problem was the presence of an amine impurity in the TBAF. This gave deprotonation to the monocation rather than the requisite anion exchange.

(30) For a recent review of spin–orbital coupling effects in tetrapyrrole derivatives, see: Bonnet, R.; Harriman, A.; Kozyrev, A. *J. Chem. Soc., Faraday Trans.*, in press.

(31) Under the same experimental conditions, the triplet lifetimes were observed to decrease in the order **1**·2HF > **1**·2HCl > **1**·2HBr (τ_t = 77, 32, and 5 μs, respectively, for these three species). This provides further support for a spin–orbital coupling mechanism. Other mechanisms, such as photoinduced electron transfer from counteranion to sapphyrin, may occur but seem unlikely to account for the observed trend in photophysical properties.

(32) Fuoss, R. M. *J. Solution Chem.* **1986**, *15*, 231–235.

(33) The time-resolved fluorescence decay profiles were analyzed according to $I_f(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where τ_1 and τ_2 refer to the fluorescence lifetimes of the ion-pair and uncomplexed species, respectively. The association constants, K_s, for the ion-pair can be expressed in the form $K_s = A_1/4C_oA_2^2$, where A_1 and A_2 respectively refer to the fractional amplitudes of the initial fluorescence attributable to the ion-pair and the uncomplexed species and C_o is the total concentration of sapphyrin present in solution. Values of K_s were calculated from the time-resolved fluorescence records for a series of C_o values.

(34) According to the Fuoss equation,[32] for a given pair of ionic reactants in dilute solution there should be a linear correlation between ln K_s and $1/\epsilon$, where ϵ refers to the bulk solvent dielectric constant at the temperature of the experiment. Inserting the appropriate values gives estimates for K_s in methanol solution for the dihydrochloride and dihydrobromide sapphyrin salts respectively of 95 and 50 M^{-1}.

(35) Using standard spin–orbital coupling theory[30] and assuming identical atomic orbital coefficients for interaction between the sapphyrin excited singlet states and the appropriate counteranion (i.e. assuming the same type IV structure for **1**·2HF as for **1**·2HCl), we calculate that the fluorescence lifetime for the dihydrofluoride salt, **1**·2HF, should be 4.1 ns, not the 5.0 ns observed by experiment.

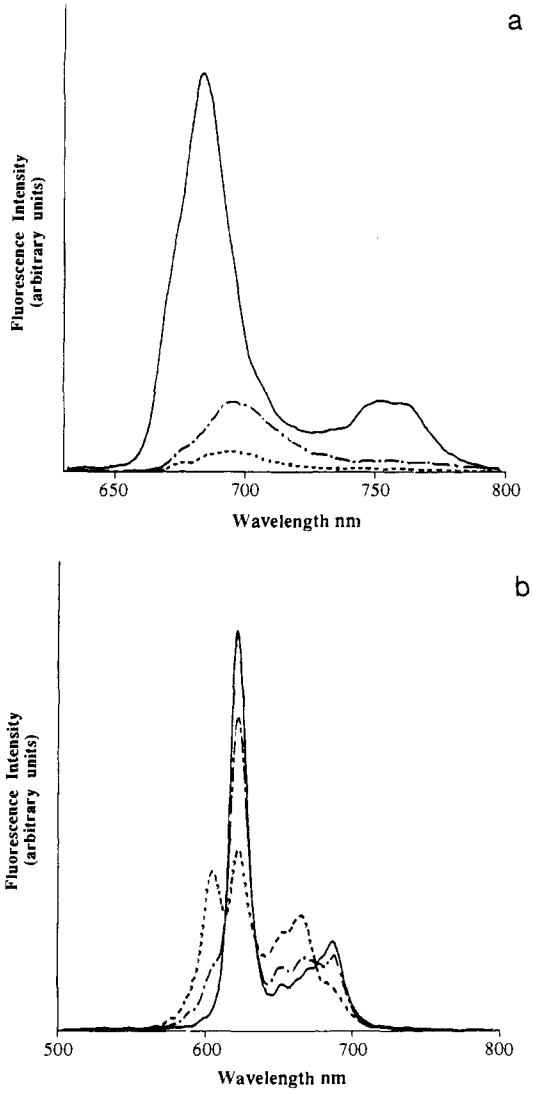


Figure 8. (a) Fluorescence spectra for the diprotonated form of sapphyrin recorded in CH_2Cl_2: (—) for the dihydrofluoride salt of **1**; (- - -) for the dihydrochloride salt of **1**; and (- · -) for the corresponding dihydrobromide salt. (b) The corresponding spectra recorded for **2**·2HF (—), **2**·2HCl (- - -), and **2**·2HBr (- · -). In all cases, the spectra were recorded in degassed CH_2Cl_2 at room temperature with excitation being carried out at the Soret maximum.

the dihydrofluoride complex of **1** show remarkable negative shifts compraed to those of the others. Namely, this fluoride complex is more difficult to reduce (by ca. 150 mV) and the reduced species is destabilized (by ca. 250 mV) in CH_2Cl_2. A similar tendency is also seen for the oxidation couples, although irreversible oxidation waves (presumably due to the oxidation of halogen anions) were observed with [**1**·2H]·2Cl and [**1**·2H]·2Br. Taken together these electrochemical results provide further evidence that the diprotonated form of sapphyrin can be considered as being a selective fluoride halide receptor in dichloromethane solution.

Conclusion

Both solid-state and solution-phase studies in CH_2Cl_2 and MeOH are consistent with the conclusion that the diprotonated form of 3,8,12,13,17,22-hexaethyl-2,7,18,23-tetramethylsapphyrin, $[\mathbf{1}\cdot 2H]^{2+}$, is capable of forming a highly stable in-cavity encapsulated complex with fluoride anion. Such in-cavity binding is not observed for any hydrohalide anion salts in the case of the smaller porphyrins; nor is it observed in the sapphyrin series for either bromide or chloride anion. Taken together, these findings are indicative that the diprotonated form of sapphyrin represents a unique and selective receptor for fluoride anion, with this observed selectivity being at least $\geq 10^3$ relative to either chloride

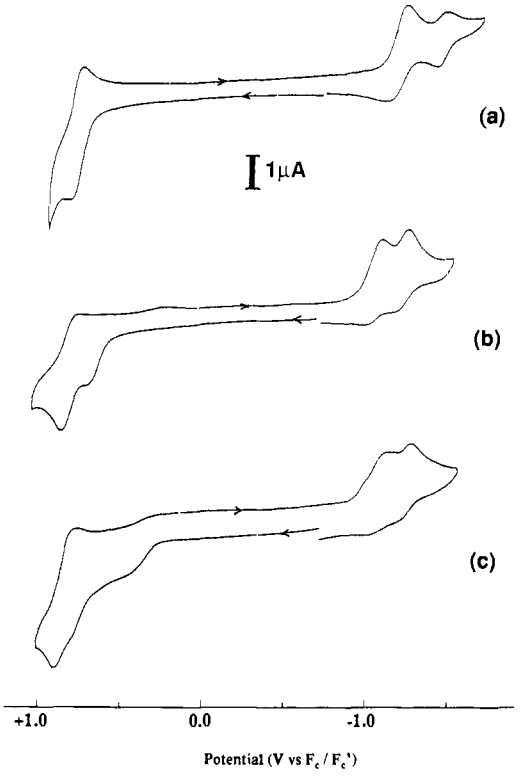


Figure 9. Cyclic voltammograms of the dihalide salts of **1** recorded under argon in CH_2Cl_2 containing 0.1 M $TBAPF_6$: scan rate = 100 mV s^{-1}; (a) fluoride, (b) chloride, and (c) bromide. The potential axis is calibrated with respect to the ferrocene/ferrocenium (F_c/F_c^+) couple (+0.72 V vs Ag/AgCl).

or bromide. Left undetermined by this study, however, is the nature of this selectivity vis à vis other anions and, indeed, the general question of whether or how such other anions might be bound.[36] Also left undetermined is the question of whether either the neutral or monoprotonated forms of sapphyrin is(are) capable of acting as anion binding agents. Nonetheless the persent results do serve to highlight the fact that suitable expanded porphyrins are capable not only of complexing large cations[37] but also of binding small anions.[38] To the best of our knowledge such strong, selective anion binding is without precedent in the porphyrin literature and could represent a new direction in porphyrin-related research. Current efforts are devoted to exploring this possibility.

Acknowledgment. Support was provided by an NIH grant (AI 28845), an NSF Presidential Young Investigator Award (1986), an Alred P. Sloan Foundation Research Fellowship (1989–1991), and a Camille and Henry Dreyfus Foundation Teacher-Scholar Award (1988–1992) to J.L.S. M.S. expresses his gratitude to Prof. E. Kimura of Hiroshima University for permitting an academic leave and to the Japanese Society for the Promotion of Science for supporting the same. We are grateful to Dr. Mike Cyr of this department for many stimulating discussions and for initial experiments related to this study. We thank both Dr. Cyr and Kaori

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(37) For an example of a large cation (UO_2^{2+}) being bound within the core of a sapphyrin derivative, see: Burrell, A. K.; Lynch, V.; Cyr, M. J.; Sessler, J. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1710–1713. For examples of other large cations being complexed by other non-sapphyrin expanded porphyrins, see for instance: (a) Sessler, J. L.; Murai, T.; Hemmi, G. *Inorg. Chem.* **1989**, *28*, 3390–3393. (b) Burrell, A. K.; Hemmi, G.; Lynch, V.; Sessler, J. L. *J. Am. Chem. Soc.* **1991**, *113*, 4690–4692. (c) Sessler, J. L.; Mody, T. D.; Lynch, V. *Inorg. Chem.* **1992**, *31*, 529–531.

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Furuta for synthetic assistance.

Registry No. 1·2HF, 136364-88-0; 1·2HCl, 136364-87-9; 1·2HBr, 141411-03-2; 1·5HF, 141411-04-3; 1·2H$^+$, 125927-22-2; F$^-$, 16984-48-8.

Supplementary Material Available: Tables of anisotropic thermal parameters for the non-H atoms, positional and isotropic thermal parameters for all atoms, bond lengths and angles, and least-squares planes and a packing diagram (14 pages); a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

Crystal Structures of Two Polymorphic Thallium(I) Salts of the Antibiotic Lasalocid A: A Polymeric Form Involving Metal–Phenyl π-Bonding and a Monomeric Form Involving the "Half-Naked" Metal Ion

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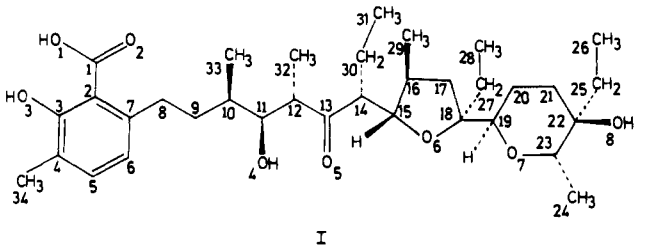
Abstract: The crystal and molecular structures of two polymorphic lasalocid A–thallium(I) salts, which were prepared from lasalocid A sodium salt and thallium nitrate, have been determined by X-ray diffraction. Salt **1**, which was crystallized from aqueous methanol, forms a one-dimensional polymer, [Tl$^+$(lasalocid A$^-$)]$_n$, where the metal ion is coordinated, on one side, to five oxygens of an ionophore molecule and, on the other side, to the phenyl ring of the neighboring molecule, with Tl–O distances of 2.678 (8)–3.363 (10) Å and a Tl–ring (centroid) distance of 3.22 Å. The coordinated oxygens are the hydroxyl O4 and O8, carbonyl O5, and ether O6 and O7. Salt **2**, which was crystallized from aqueous methanol–ethylene glycol, forms a monomer, Tl$^+$(lasalocid A$^-$), where the metal ion is coordinated, on one side, to six oxygens of an anion ligand with Tl–O distances of 2.618 (8)–3.202 (8) Å. The coordinated oxygens involve the carboxylate O2 in addition to the five oxygens in **1**. The other side of the metal ion is completely naked and exposed to a nonpolar environment provided by hydrophobic alkyl groups of neighboring molecules in the crystal structure. This is the first ionophore–metal complex that lacks three-dimensional nonpolar enclosure of the metal ion. In both salts, the conformational rigidity of the lasalocid A anion molecule is preserved: the pseudocyclic conformation is stabilized by "head-to-tail" O1···H–O8 and also by O2···H–O4 hydrogen bonds, with most of the polar oxygens directed inward to capture the metal ion and with all nonpolar groups outward. The formation of two polymorphic structures under similar crystallization conditions indicates that the Tl$^+$–phenyl η^6-bonding in salt **1** is weak. Crystallographic details: for **1**, Tl$^+$($C_{34}H_{53}O_8^-$), space group $P2_12_12_1$, a = 22.851 (2) Å, b = 11.320 (1) Å, c = 13.790 (2) Å, V = 3567.1 (8) Å^3, Z = 4, R_F and R_{wF} of 0.056 and 0.036, respectively, for 2573 reflections with $F_o > 5\sigma(F_o)$; for **2**, Tl$^+$($C_{34}H_{53}O_8^-$), space group $P2_12_12_1$, a = 18.928 (5) Å, b = 18.649 (6) Å, c = 10.054 (1) Å, V = 3549 (1) Å^3, Z = 4, R_F and R_{wF} of 0.048 and 0.028, respectively, for 2041 reflections with $F_o > 5\sigma(F_o)$.

A structural principle of ionophore–metal complexes not only for naturally occurring ionophores[1] but also for synthesized ones[1b] such as crown ethers, cryptands, or podands is that ionophores entrap charged hydrophilic metal ions with the hydrophobic side chains of the ionophore being oriented toward the periphery of the molecule. This provides effective screening of the central cation from solvent interactions and facilitates solubilization of metal ions into nonpolar media in the presence of ionophores. This is the basis of the function of ionophores as complexation and transporting agents for metal ions through lipophilic membranes. Lasalocid A (I), a carboxylic acid-type polyether antibiotic, is one of the first representatives of the naturally occurring ionophores.[2] It is unique in both its structure and its function: it is relatively small and contains an aromatic ring with a salicylic acid moiety, and it possesses the ability to complex and transport mono-, di-, and even trivalent cations through natural and artificial membranes, thus attracting the attention of numerous investigators, resulting in a large body of data on its biology[3a] and chemistry.[3b] Indeed, lasalocid A is one of the ionophores which has most extensively been subjected to X-ray crystallographic studies;[1] these include free acids,[4] amine complexes,[5] and metal salts such as those of Na$^+$,[6a-c] Ag$^+$,[6d-f] Cs$^+$,[6i] and Ba^{2+}.[6g,h] Usually, lasalocid A forms



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