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The Preparation, Properties and some Simple Reactions of $[Fe(TPP)]^+SbF_6^-$

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$[Fe(TPP)]^+ SbF_6^-$ can be prepared from Fe(TPP)·Br or Fe(TPP)·Cl by the action of $AgSbF_6$ in dry dichloromethane. Mössbauer and susceptibility measurements indicate a $S = 3/2$ ground state. Reactions with various nucleophiles are described.

Introduction

We wished to prepare ferric tetraphenyl porphyrin as a cation free of axial ligands in order to investigate its reactions with potential oxidizing agents free of complicating side-reactions, such as the prior displacement or oxidation of X^- in compounds Fe TPP X (typically $X = Br^-$ or Cl^-). Noting the propensity of perchlorates to include water of crystallisation or of co-ordination, and to explode, we prepared the hexafluoroantimonate of the ferric tetraphenyl porphyrin cation. This salt is free of solvent of crystallisation [1] or co-ordination [2] and is freely soluble in non-donor polar solvents like dichloromethane, and in solvated form is very soluble in donor solvents (*e.g.* d.m.s.o.) and we here describe its preparation and some properties.

Experimental

Solvents

Dichloromethane was refluxed over calcium hydride and distilled prior to use, as was methanol. Acetone was dried over 'Drierite' and distilled prior to use, and benzene was refluxed over sodium wire and distilled prior to use. All glassware was oven dried.

Analyses

Were performed by Midwest Microlabs Inc. Skokie, Illinois and Dr. Strauss, Oxford.

$TPPH_2$

α, β, γ, δ meso tetraphenylporphyrin was prepared from pyrrole and benzaldehyde in refluxing propionic acid, after Adler [3]. It was freed from chlorine (~3% by Badger's method [4]) by the procedure of Smith [5] using dichlorodicyanoquinone (Kodak).

FeTPPCl

The chromatographically pure tetraphenylporphin (*Anal.*: Required C 86.0, H 4.89, N 9.12. Found C 85.74, H 4.70, N 9.07) was then converted to its ferrichloride by the method of Rothemund and Menotti [6], and freed of traces of μ-oxo-dimer by chromatography [7]. *Anal.*: Required C 75.05, H 3.98, N 7.96, Fe 7.96, Cl 5.05. Found C 74.4, H 3.8, N 7.79, Fe 7.95, Cl 5.71. μ_{eff} (20 °C) = 5.95 BM. νFe–Cl = 380–560 cm^{-1}.

$FeTPP_2O$

In a typical preparation 0.62 g of FeTPPCl was dissolved in 100 ml of CH_2Cl_2, twice shaken with 4 *N* KOH solution, the CH_2Cl_2 layer was separated, dried over solid KOH, then over Woelm alumina and finally passed through a 3″ Woelm alumina column. The solvent was evaporated, then the residue dissolved in benzene, the solution concentrated and allowed to cool. The μ-oxo-dimer which crystallised out was dried at 100 °C. Yield 75%, ν Fe–O–Fe, 870 cm^{-1}.

FeTPPBr

This was prepared from the μ-oxo-dimer. In a typical preparation 0.08 g of $(FeTPP)_2$ was dissolved in 70 ml of CH_2Cl_2, twice shaken with 100 ml of 48% HBr, then with 100 ml of water, the CH_2Cl_2 layer was dried over sodium sulphate, concentrated, and some MeOH added. The resulting crystals were separated by filtration, washed with water, then methanol, and dried over P_2O_5 in a desiccator (ν Fe–Br = 280–300 cm^{-1}).

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*TPP = The dianion of α β γ δ meso tetraphenyl porphyrin. OEP = The dianion of octaethyl porphyrin.

FeTPP$^+$SbF$_6^-$

Was prepared from FeTPPCl and FeTPPBr. In a typical preparation from FeTPPCl, 0.69 g of AgSbF$_6$ (Ozark-Mahoning) were weighed into a stoppered bottle in a glove-box under dry nitrogen, and were dissolved in 25 ml of dried CH$_2$Cl$_2$, Then 1.41 g of FeTPPCl, an equimolar amount, was weighed out and dissolved in 150 ml of CH$_2$Cl$_2$. The silver ion solution was added to the brown solution of ferrichloride and a precipitate of silver chloride and an orange-red solution resulted. The reaction mixture was allowed to stand for ten minutes and then the silver chloride was removed using a no. 4 sintered glass filter-funnel. The filtrate was treated with dry benzene and a glistening purple precipitate resulted. Further crystals were obtained as the more volatile CH$_2$Cl$_2$ evaporated. Recrystallisation could be effected from 90% benzene 10% dichloromethane with exclusion of moisture and the crystalline product was dried at 70 °C for four hours. Yield 78%. *Anal.*: Required for FeTPP$^+$SbF$_6^-$: C 58.4, H 3.1, N 6.2, Fe 6.2, Sb 13.5, F 12.6. Found, C 57, H 3.1, N 5.9, Fe 6.1, Sb 9.4, F 12.2. A later-prepared sample had: C 58.0%, H 3.1, N 6.0, Fe 6.6, F 12.9. Field desorption mass spectrometry shows a stable molecular ion [FeTPPSbF$_6$]$^+$ at 903 and additional stable ions corresponding to [FeTPPF]$^+$ and [FeTPP]$^+$.

Measurements

Field-desorption mass-spectral measurements employed a V.G. Micromass ZAB-1F mass spectrometer. U.V./visible measurements were made on a Perkin Elmer 124 instrument with molar extinction coefficient measurements determined on a Perkin Elmer 555 instrument. I.R. measurements from 4000–200 cm^{-1} using Nujol mulls and KBr discs employed a Perkin Elmer 357 instrument. Magnetic measurements (Faraday) were made on a magnetic balance of Prof. R. H. Holm; Mössbauer and variable temperature measurements were kindly performed by Prof. Frankel at the Francis Bitter National Magnet Laboratory. Measurements at stationary and rotating platinum electrodes were carried out in dry dichloromethane solvent using 10^{-2} *M* (n-hexyl)$_4$N$^+$ SbF$_6^-$ as supporting electrolyte, and a Princeton Applied Research 174 polarographic analyser.

Results and Discussion

The method of synthesis, analytical results and mass spectrum all confirm the production of FeTPP$^+$ SbF$_6^-$. The i.r. spectra of the solid show absorptions characteristic of MTPP (C–H stretch at 3040 cm^{-1}, C=N stretch at 1595 cm^{-1}), no absorption for FeCl/FeBr or Fe–O–Fe, but two strong absorptions characteristic of SbF$_6^-$ at ν_2 (665 cm^{-1}) and ν_5 (290 cm^{-1}) [8]. In dichloromethane, freshly dried acetone, glacial acetic acid or dry benzene the compound has the same u.v./visible spectra with a Soret band at 405 nm (ϵ_m = 6.37 × 10^4 cm^{-1} *M*$^{-1}$) and visible bands at 635 nm (1.12 × 10^3), 667 nm (1.37 × 10^3); this is similar to but not identical with, FeTPPX species. In view of the changes in spectrum which occur with anions and nucleophilic solvents, it seems probable that dichloromethane, benzene, acetone and glacial acetic acid do not co-ordinate to the FeTPP$^+$ cation.

FeTPPCl can be oxidised in two steps at a rotating Pt electrode in CH$_2$Cl$_2$ with (n hexyl)$_4$N$^+$SbF$_6^-$ or PhCH$_2$NEt$_3^+$SbF$_6^-$ as supporting electrolyte, each oxidation wave being of equal height, with E$_{1/2}$ (*vs.* S.C.E.) values of 1.07 v and 1.54 v, in close agreement with Felton *et al.* [1]. The FeTPP$^+$SbF$_6^-$ oxidation waves were also of equal height and at similar half-wave potentials, 1.11 v and 1.46 v and it is reasonable to suppose that the first wave involves iron oxidation, the second ring oxidation, as with FeTPPCl; this point could be settled by use of an optically transparent thin layer electrode.

An interesting question concerns whether or not the SbF$_6^-$ ion is bonded to the central ion atom, possibly by a fluoride bridge – a question which can only be answered unequivocally by diffraction methods. In the corresponding perchlorate diffraction methods indicate weak bonding between one perchlorate oxygen and the central iron atom [2], with evidence of this appearing in the infrared [2, 9]. here is no infrared evidence of this bonding in the hexafluoroantimonate. The magnetism of the perchlorate [2, 10] has been held to indicate a quantum mechanical mixture of S = 3/2 and S = 5/2 spin states, with the lowest energy Kramers' doublets having more S = 3/2 character. Thus in the solid state and in solution μ_{eff} falls with temperature from μ = 5.1 at 298 K to 4.1 at 40 K. In our case the room temperature (298 K) moment is 4.27 ± 0.02 B.M. and susceptibility measurements down to 1 K denote no change in spin state. In general our room temperature moment is about 1 B.M. lower than for the related compounds FeTPP$^+$SbF$_6^-$·5THF (5.3 B.M.) [10], FeTPP$^+$PF$_6^-$·5THF (5.2 B.M.) [10] and FeTPP$^+$BF$_4^-$·2THF (5.2 B.M.) [10] and FeTPP$^+$C(CN$_3$)$^-$ (5.4 B.M.) [13]. The Mössbauer spectrum of the hexafluoroantimonate is a single widely spaced doublet (at 77 K, δFe = 0.289 mm s^{-1}, ΔE_Q = 3.458 mm s^{-1}) and this and the susceptibility indicate a single spin state, S = 3/2, with a strong tetragonal field at the iron atom. The difference between our hexafluoroantimonate and related compounds is most probably that in ours, the iron is in a true square planar environment, whereas solvent molecules or anions are bonded axially to iron in the related compounds.

TABLE I. Reactions of $[Fe(TPP)]^+SbF_6^-$.

Reagent	U.v./visible spectrum of product (maxima) (nm)	Porphyrin Compound formed
D.M.S.O. (Me_2SO)	400, 415, 495, 530, 655, 683	$[Fe(TPP)\cdot(dmso)_2]^+SbF_6^-$
H.M.P.A. ($(NMe_2)_3PO$)	422, 495, 530, 650, 690	$[Fe(TPP)(hmpa)_2]^+SbF_6^-$
Pyridine	415, 520 545 max, 580 sh	$[Fe(TPP)py_2]^+SbF_6^-$
Dry EtOH	500, 530, 660, 690	$[Fe(TPP)(ROH)_2]^+SbF_6^-$
Dry MeOH	500, 530, 660, 690	
Wet acetone	500, 530, 690	$[Fe(TPP)(H_2O)_2]^+SbF_6^-$
C_6H_5CN	545, 565, 667	$[Fe(TPP)(PhCN)_2]^+SbF_6^-$
MeOH + OMe^-	Broad plateau, centred on 600 nm, (sh) at 480 nm	Fe(TPP)·OMe
EtOH + OEt^-	500 (sh), 575 (max), 620 (br,sh)	Fe(TPP)OEt
HOAc + OAc^-	508, 572, 680	Fe(TPP)·OAc
Cl^-	375/413, 510, 575, 660, 690	Fe(TPP)·Cl
Pyridine + Cl^-	510, 530, 585, 660, 695	Fe(TPP)(py)Cl
Acetone + OH^-	408, 570, 610	$[Fe(TPP)]_2O$

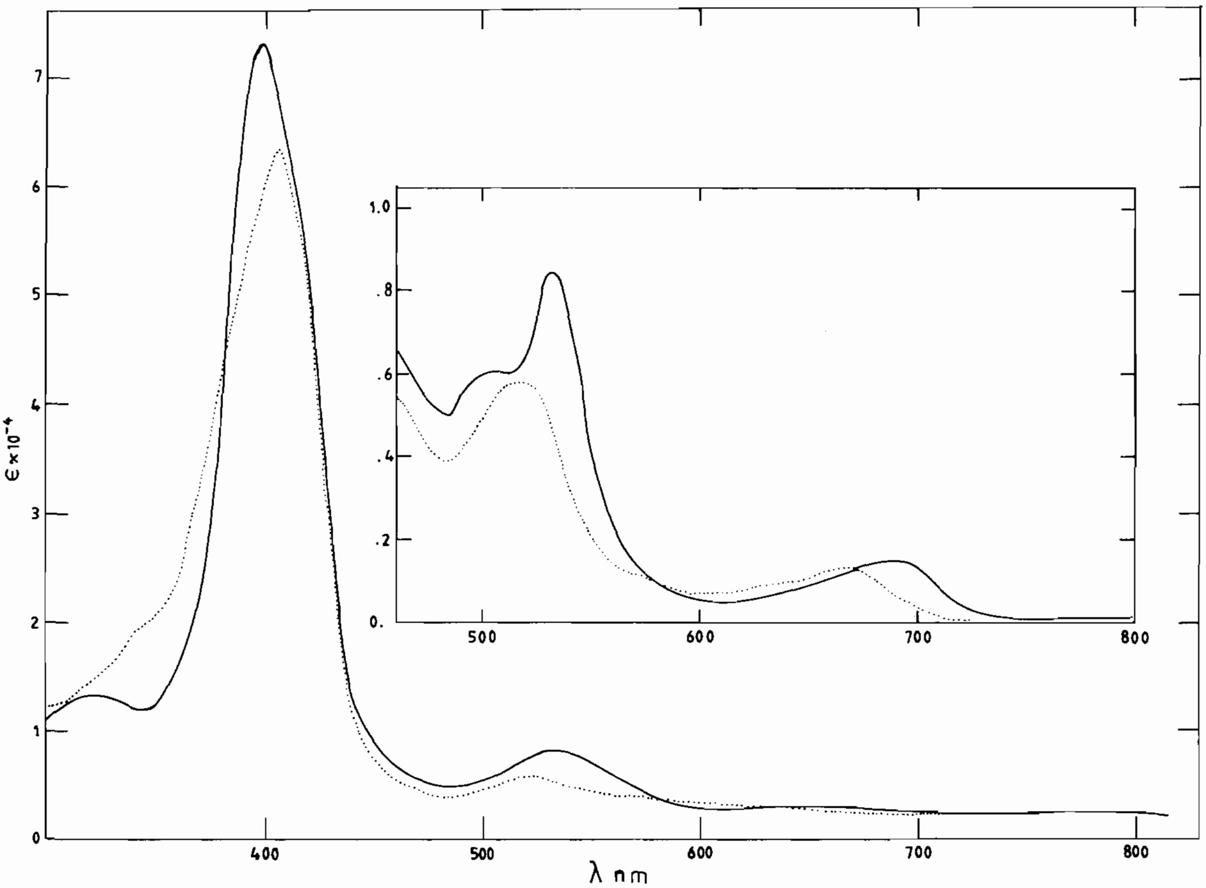

Fig. 1. Absorption spectra for $FeTPP^+SbF_6^-$. (i) Dotted line: $FeTpp^+SbF_6^-$ in CH_2Cl_2. (ii) Continuous line: one drop DMSO added to (i).

Solution Properties

If solutions of co-ordinating solvents in acetone or dichloromethane or quaternary ammonium salts in acetone or dichloromethane are added to a solution of $FeTPP^+SbF_6^-$ in dichloromethane or benzene, the spectrum of $FeTPP^+$ changes and becomes characteristic of $FeTPP^+$ $(solvent)_{1\,or\,2}$ or FeTPP (anion) species, and in most cases direct comparison can be made with authentic samples. Reduction of a CH_2Cl_2 solution of $FeTPP^+$ by aqueous alkaline dithionite in the presence of pyridine produces the stable pyridine haemochrome, $FeTPP(py)_2$, again indicating the integral $FeTPP^+$ unit in $FeTPP^+SbF_6^-$. Contact with hydroxide solution produces μ-oxo dimer. The spectroscopic changes and reactions are summarised in Table I.

Several comments can be made. Firstly, the donor solvents d.m.s.o., h.m.p.a., water (in acetone), ethanol and methanol all produce very similar spectra with a dominant peak in the visible region at 530 nm (Fig. 1).

The compound $[FeTPP(dmso)_2]^+(ClO_4)^-$ has been prepared [9] and has a spectrum identical to that of $FeTPP^+SbF_6^-$ in d.m.s.o., and in the perchlorate axial attachment of d.m.s.o. oxygen has been confirmed by diffraction [11]. $FeTPP^+(EtOH)_2BF_4^-$ has been prepared and its structure confirmed, but no spectrum has been given [12]. Methoxides of Iron(III) porphyrins have been described [14, 15] and the spectrum of FeOEP(OMe) [15] is very similar to that we have ascribed to FeTPPOMe. Addition of acetate ion to a glacial acetic acid solution of $FeTPP^+SbF_6^-$ changes the spectrum to that of the acetate, FeTPPOAc. The reactions of chloride solution and of moist acetone are identical to those described by Goff [16] for $FeTPP^+ClO_4^-$. A reaction mixture of $FeTPP^+SbF_6^-$, pyridine and *p*-nitrobenzyl pyridinium chloride gives a spectrum identical to that observed by Fleischer [7] from the initial dissolution of FeTPPCl in pyridine, and this spectrum is ascribed to FeTPP·py·Cl (Fleischer [7] ascribed this spectrum to $(FeTPPpy_2)^+Cl^-$, but that spectrum would clearly be almost identical with that of $FeTPPpy_2^+SbF_6^-$, which is different, and can be obtained by dissolving $FeTPP^+SbF_6^-$ in pyridine).

The Action of Superoxide Ion

Ferrous porphyrin plus oxygen is formally equivalent to ferric porphyrin plus superoxide, and ligand-free $FeTPP^+$ appeared a favourable substance to study in this connection. One report [17] involves the addition of superoxide to $\{Fe(protoporphyrin\ IX\ dimethyl\ ester)\}^+\ ClO_4^-$ in d.m.f. at –50 °C and an Iron(III) superoxide complex which on warming gives an Iron(II) complex with (presumably) co-ordinated D.M.F., and the second [18] reveals a complex series of reactions in d.m.s.o./toluene/crown ether mixtures, involving Fe(III)(TPP or OEP)Cl and potassium superoxide. However, we have discovered that dicyclohexyl-18-crown-6 reacts with $FeTPP^+SbF_6^-$ in benzene to give a FeTPPX spectrum; $(18\text{-crown-}6)_2CH_3CN$ reacts in benzene with $FeTPP^+SbF_6^-$ to give an orange-red precipitate, which precipitate will dissolve in dry acetone to give an FeTPPX spectrum also. For these reasons it was decided to dispense with crown ether and react $FeTPP^+SbF_6^-$ in a non nucleophilic solvent with KO_2 in d.m.s.o. solution, as d.m.s.o. will dissolve to form up to 10^{-2} *M* superoxide solution. In d.m.s.o. at room temperature the addition of small successive amounts of superoxide solution gave a product with a Soret band at 418 nm, and visible absorption maxima at 570, 595 and 610 nm. Authentic $(FeTPP)_2O$ in d.m.s.o. has a Soret band at 408 nm, unaffected by superoxide, and further bands at 570 and 610 nm, so the end solution could contain some μ-oxo-dimer, as from the decomposition of $Fe(II)O_2$, plus at least one other product. During the course of reaction the Soret band moves from 415/400 (twin peaks) to 427 nm and then to 418 nm, with an occasional not-always reproducible peak at 435 nm on addition of excess superoxide. Similar results were observed on the addition of potassium superoxide/d.m.s.o. solutions to $FeTPP^+SbF_6^-$ in solvents benzene, toluene and dichloromethane. According to Valentine and others, the Soret band at 427 nm is characteristic of $FeTPP(d.m.s.o.)_2$ so that at room temperature the initial reaction would appear to be:

$$[FeTPP(d.m.s.o.)_2]^+ + O_2^- \rightarrow O_2 + FeTPP(d.m.s.o.)_2$$

The eventual product would appear to be μ-oxo-dimer (though the shift in the Soret peak from 408 to 418 is worrying) and possibly the μ-peroxo complex, $[Fe(III)\ peroxide]^-$, described by Valentine as resulting from the action of superoxide on $Fe(II)TPP(d.m.s.o.)_2$, which has a Soret band at 435 nm, and visible peaks at 566, 595 and 610 very similar to, but not identical with, these of $(FeTPP)_2O$. Obviously work at low temperatures needs to be performed to isolate intermediates and to clarify the role of crown ethers other than as facilitators of superoxide dissolution.

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