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An adduct of Hydrogen Bromide and Ferrous Phthalocyanine

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Ferrous phthalocyanine (FePc) and concentrated hydrobromic acid react giving a 1:1 FePc–HBr adduct. In aprotic solvents adduct formation is reversable and is a reaction of bromide ion with protonated phthalocyanine.

Introduction

Hydrochloric acid reacts with ferrous phthalocyanine to produce a compound which is an adduct of ferrous phthalocyanine and hydrogen chloride with iron most probably in the ferrous state,[1,2] though the compound was formerly called « Chloroferric phthalocyanine ».[3] Mössbauer results[4] suggest that it is unlikely that this solid compound contains ferric iron, or is a hydride of Fe^{IV}. We report here the reaction of hydrogen bromide with ferrous phthalocyanine, and some properties of the adduct.

Experimental Section

Ferrous phthalocyanine was made by the method of Meloni, Ocone and Block[5] and analysed thus. Found: C, 67.6; H, 2.8; N, 19.7; Fe, 9.8. Required for $FeC_{32}H_{16}N_8$: C, 67.5; H, 2.9; H, 19.9; Fe, 9.8.

HBr Adduct. Ferrous phthalocyanine (0.81 g) was heated with 80 ml of concentrated « Analar » hydrobromic acid on a water bath for 2 hours. The lustrous purple needles of β ferrous phthalocyanine broke up producing a black micro-crystalline solid which was collected on a sintered glass funnel and washed with water until the washings were acid-free, with alcohol until the green washings became colourless, and then with acetone until the brown-green washings became very pale green. The black microcrystalline solid was then dried for 24 hours *in vacuo* over phosphorus pentoxide. Yield 0.82 gm. Found: C, 59.0; H, 2.8; N, 17.2; Fe, 8.5; Br, 12.4. Required for $FeBrC_{32}H_{17}N_8$: C, 59.2; H, 2.6; N, 17.3; Fe, 8.6; Br, 12.3.

Removal of HBr with pyridine. The hydrobromide described above (0.50 g) was refluxed with (« A-nalar ») pyridine for 20 minutes, during which time a purple crystalline solid formed. The crystals were filtered off, washed with a little benzene and dried in a vacuum dessicator over potassium hydroxide pellets. These crystals dissolved in acetone had a spectrum identical to that of an authentic sample of the bis-pyridine adduct of ferrous phthalocyanine, FePc-$(py)_2$. Found: N, 19.0; Br, 0.0. Required for FePc-$(py)_2$: N, 19.3; Br, 0.0.

(Analyses were performed by Alfred Bernhardt, Mülheim, West Germany).

Dimethyl sulfoxide and dimethyl acetamide were purified by vacuum fractionation from calcium hydride, as already described.[6] Visible spectra were run on Perkin Elmer 124 and 450 instruments, the latter instrument being able to accommodate variable short pathlength cells. Diffuse reflectance spectra were run on a Unicam SP800B instrument fitted with a diffuse reflectance accessory, a scale expansion unit and an external recorder. Mulls in silicone grease were smeared on filter paper and run against a filter paper reference, smeared with the same grease. Control experiments showed that the grease had no effect on peak positions.

Infrared spectra were run on Perkin Elmer 137 and 225 instruments, in Nujol mulls and KBr discs. Far infrared spectra were run in polyethylene discs on an R.I.I.C. interferometer.

Magnetic measurements on solid samples were made at room temperature (18°C) on a simple Stanton-Newport Guoy balance. Evans'[7] method was used for magnetic measurements in solution. A Perkin Elmer 60 MHz «R10» spectrometer was used at 33°C, and the measurements of magnetic moment in solution are accurate to no more than *ca.* ±0.2 BM because of the insolubility of the hydrobromide. The most concentrated solutions used were $< 10^{-3}$ *M*, and their concentrations were determined by dilution with pyridine and measuring the absorbance at 654 nm of the $FePc(py)_2$ complex. Such solutions gave a separation of only 0.5 Hz between internal and external T.M.S. signals.

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Results and Discussion

a. The Solid. The solid product from treating ferrous phthalocyanine with hydrobromic acid has the following properties.

(1) It has a 1:1 iron to bromine ratio.

(2) It is black, and has a different diffuse reflectance spectrum (Fig. 1) from ferrous phthalocyanine; its diffuse reflectance spectrum is like that of ferrous phthalocyanine hydrochloride.

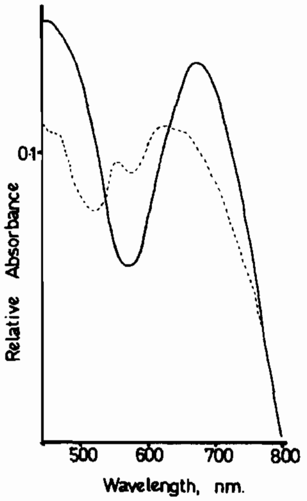

Figure 1. Diffuse reflectance spectrum of FePc . HBr ——— and the diffuse reflectance spectrum of FePc – – –.

(3) Above 400 cm^{-1} its infrared spectrum is very like that of ferrous phthalocyanine and its hydrochloride, differences being small ones of relative peak height, with the exception of weak additional peaks at 1550 cm^{-1} 925 cm^{-1} and 800 cm^{-1}. No N—H frequencies were detected, just as we have not been able to detect them in the hydrochloride. There have been reports that these frequencies can be detected when thin films of ferrous phthalocyanine have been exposed to acid vapours.[8]

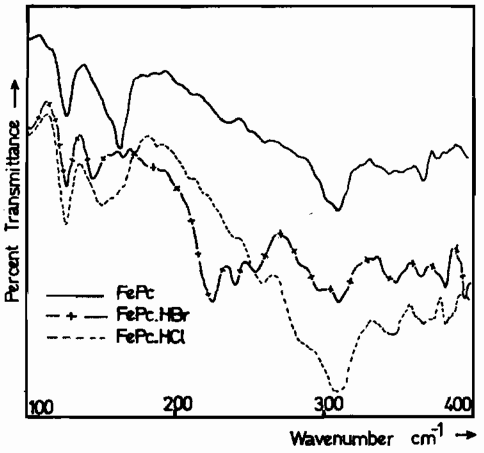

Figure 2. Far i.r. spectra of FePc, FePc . HCl and FePc . HBr.

Below 400 cm^{-1} (Fig. 2), the strongest absorption is that at 310 cm^{-1}, common to FePc, FePc . HCl, and FePc . HBr. We suggest, by analogy with the metalloporphyrins,[9] that this may be an Fe—N stretching mode coupled to a ring deformation. Its absence in PcH_2 and Li_2Pc would seem to confirm the assignment. This absorption is strongest of all in FePc . HCl, and it may be that Fe—Cl stretching adds to the intensity here. The hydrobromide itself has a very strong absorption at 224 cm^{-1}, and this might be assigned to a mode containing Fe–Br stretching; it has been so assigned in $Fe^{II}(Di\text{-}2\text{-}pyridylamine)_2Br_2$.[10]

(4) The room-temperature magnetic moment of the hydrobromide is 3.9 BM, 0.1 BM above that of ferrous phthalocyanine[4] and higher than that of the hydrochloride, 3.3 BM.[11] Low temperature magnetic[4] and Mössbauer[4] studies on these latter two compounds pointed to their both having a triplet ground state, and not being ferrous complexes with a singlet ground state and an easily accessible quintet state. Such studies on the hydrobromide would be interesting and are in hand.

b. Solution Studies. When a small amount, *e.g.* .025 ml of a concentrated filtered solution of the hydrogen bromide adduct (*ca.* 10^{-3} *M*) in DMSO is diluted with, say 2.5 ml of DMSO the spectrum seen initially is shown in Fig. 3, with maxima at 550, 535 and 675 nm. If care has been taken to exclude traces of acid from the system the spectrum slowly reverts to that of $FePc(DMSO)_2$. In DMA the hydro-

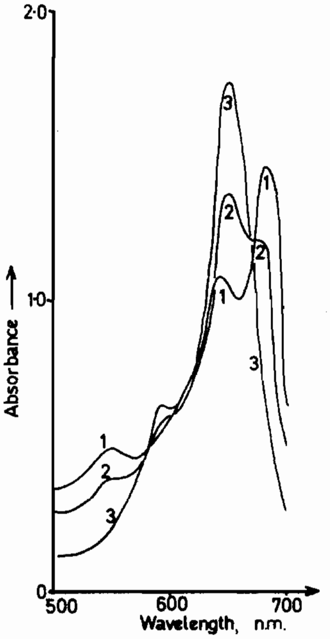

Figure 3. Visible spectrum of FePc . HBr freshly made up in DMSO. (1, 2 and 3 are at increasing time intervals after diluting a concentrated FePc . HBr/DMSO solution).

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gen bromide adduct has the same spectrum as the initial one in DMSO, but does not change unless base is added. The formation of bis-base adducts of ferrous phthalocyanine from hydrogen halide adduct solutions and added base in these solvents is not instantaneous, and we intend to study the kinetics of these reactions further.

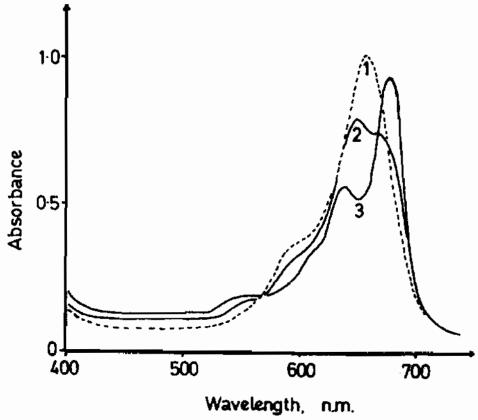
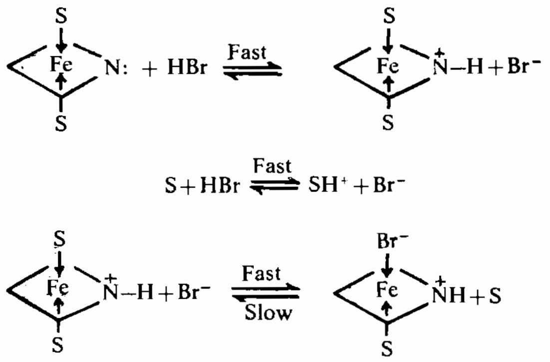


Figure 4. Successive additions of HBr gas to FePc in DMSO. (1, 2 and 3 represent spectra after successive additions of HBr).

Fig. 4 shows the sequence of changes when a fresh solution of hydrogen bromide in DMSO is added in successive increments to a *ca.* 10^{-5} *M* solution of ferrous phthalocyanine in DMSO. These changes are the reverse of those shown in Fig. 3, and can be paralleled in DMA. Unlike the reverse changes, they are « instantaneous ». As previously described with hydrogen chlorides[1,2] the simplest explanation of these changes is in terms of a reversible addition of hydrogen bromide to ferrous phthalocyanine,

$$FePc(DMSO)_2 + HBr \rightleftharpoons FePc \cdot HBr + 2DMSO$$

If careful steps are taken to exclude all traces of acids, in both DMSO or DMA, addition of bromide or chloride ion to ferrous phthalocyanine produces no change in spectrum. In the presence of even a trace of strong acid, the spectrum of the HBr or HCl adducts is seen at once. So the formation of the halogen acid adducts is best described as an attack of halide ion on protonated ferrous phthalocyanine. Halide ions do not react with the unprotonated complex. Denoting FePc by the diamond symbol below, with one bridging azamethine group shown, and the solvent by S, we can write the sequence as:



In previous publications[1,2] on the hydrogen chloride adduct it was noted that in DMSO solution this adduct was diamagnetic, and $FePc(DMSO)_2$ was also diamagnetic in solution.[6] The slow loss of HCl from the adduct to form $FePc(DMSO)_2$ was explained in terms of a rate determining exchange of Cl^- for DMSO at a low-spin d^6 Fe^{II} centre, followed by rapid proton loss from a protonated azamethine bridge.

Magnetic moment measurements by Evans' method in the case of the hydrogen bromide adduct show a different pattern, in that a freshly prepared and filtered solution of the HBr adduct concentration *ca.* 10^{-3} *M* is paramagnetic in both DMSO (2.5 BM) and DMA (3.0 BM). Transformation to bis-base adducts must thus involve a spin change in this case, and such transformations deserve further study both from kinetic and magnetic viewpoints, although the small concentrations used make precise magnetic measurements difficult.

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