Residual Paramagnetism in Silver(III) Metalloporphyrin Complexes

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Silver(III) metalloporphyrin complexes, $Ag^{III}P$ [where P = octaethylporphyrin (**1**), *meso*-tetraphenylporphyrin (**2**), *meso*-tetra(2,4,6-trimethoxyphenyl)porphyrin (**3**)] were unexpectedly found to contain residual paramagnetism owing to the presence of $Ag^{II}P$ in small amounts; the possibility of generating molecular conductors and semiconductors, based on silver metalloporphyrin complexes, is examined.

Silver(II) metalloporphyrin complexes have been well characterised,[1] especially by e.s.r. spectroscopy.[2] Apart from homogeneously catalysing the electrochemical reduction of CO_2,[3a] their chemistry shows few notable features,[3b] except for the facile oxidation[4] of Ag^{II} porphyrins, at the metal centre, to the comparatively rare silver(III) complexes.[5] This can be achieved chemically, electrochemically, or *via* pulse radiolysis.[4c] According to magnetic susceptibility measurements and e.s.r. spectroscopy,[4a] isolated (**1a**) is stable and diamagnetic, as expected for a square-planar d^8 metalloporphyrin complex (*e.g.*, Pd^{II} and Pt^{II}).[6] We now report, however, evidence for the formation of persistent $Ag^{II}P$ paramagnetism in some Ag^{III} metalloporphyrin complexes, which we propose could ultimately act as the basis for new types of molecular conductors and semiconductors.

Silver was inserted into the three porphyrins (**1**)—(**3**), and the resulting Ag^{II} complexes were oxidised *via* literature methods.[4b,7] After work-up, the chromatographically pure $Ag^{III}P$ porphyrins were evaporated to dryness and used without further purification.

During a recent study of one-bond ^{13}C–$^{1}H_{methine}$ (^{1}J) n.m.r. coupling constants in diamagnetic metallo-OEP (OEP = octaethylporphinato) complexes,[8] the ^{1}H and ^{13}C n.m.r. spectra of (**1a**) were found to be broadened. This suggested the presence of some paramagnetic impurity. T.l.c. of the (**1a**) n.m.r. sample gave two spots, one at the base-line and another with the same R_f value as Ag^{II} OEP (**1b**). Freshly prepared (**1a**), however, showed no trace of (**1b**) by t.l.c., but on standing, either as the solid or in solution, gave two spots. Redevelopment of the t.l.c. plate after drying, indicated that more (**1b**) had been formed. The same behaviour was noted for all the Ag^{III} porphyrin samples. The presence of $Ag^{II}P$ in the moving spot was confirmed by e.s.r. spectroscopy.

In dichloromethane solutions ($\sim 10^{-1}$ M), e.s.r. revealed weak multiline spectra with g-values ($<g>$), hyperfine splitting constants ($<a>$ and $<a_N>$) and line-widths (ΔH_{pp}) indicative of the $Ag^{II}P$ X-band region[2] (see Table 1). This is due to two sets of overlapping nonets, from the interaction of $^{107,109}Ag$ ($S = \frac{1}{2}$) with the four porphyrin nitrogens ($S = 1$).

Solid-state e.s.r. spectroscopy of the Ag^{III} complexes also showed multiline spectra reminiscent of polycrystalline $Ag^{II}P$ (see Table 1). Our e.s.r. parameters for Ag^{II} TPP (TPP = tetraphenylporphinato) differs slightly from those in the literature probably because of the nature of the surrounding diamagnetic matrix. Manoharan and Rogers[2] use $Ag^{II}TPP$ doped into free-base H_2TPP, while in our work, the $Ag^{II}TPP$ can be considered as doped into (**1a**). The solid-state e.s.r. spectra also show a more intense line, absent in the solution spectra, superimposed on, and to high field of, the weak $Ag^{II}P$ multiline spectra, which disappeared over several months. This suggests either the presence of long lived radicals in the solid state, or delocalisation of electron density over several macrocyclic units. Contrary to previous reports[4a,b] therefore, Ag^{III} metalloporphyrins appear to contain small amounts of the paramagnetic Ag^{II} species. This could result from electron reorganisation between the Ag^{III} cation and the porphyrin

Table 1. Experimentally-determined e.s.r. *g*-values, splitting constants, and line-widths.[a]

	Solution (CH_2Cl_2)			Polycrystalline		
	$<g>$	$<a>$	$<a_n>$[b]	$g\perp$	A	A_N
(1a)		Trace		—	49 ± 4	26 ± 3
				singlet has $g = 2.008 \pm 0.2$ and $\Delta H_{pp} = 4.9 \pm 0.4$[b]		
(2a)	2.064 ± 0.002	44.3 ± 0.5	22.1 ± 0.5	2.049 ± 0.002	49 ± 2	27 ± 2
		ΔH_{pp} 9.6 ± 0.5		singlet has $g = 2.009 \pm 0.002$ and $\Delta H_{pp} = 5.7 \pm 0.5$		
	2.0603 ± 0.0005	42.73 ± 0.5	22.93 ± 0.1	(2.032 ± 0.001)	(57 ± 0.5)	(21 ± 0.3)[c,d]
(3a)	2.063 ± 0.005	44 ± 2	22 ± 2	2.032 ± 0.002	50 ± 2	24 ± 2
		ΔH_{pp} 10 ± 2			ΔH_{pp} 14.3 ± 0.7	
				triplet has $g = 2.009 \pm 0.002$; $a' = 7.3 \pm 0.5$;		
					$\Delta H'_{pp}$ 4.6 ± 0.5	

[a] E.s.r. spectra were recorded on a Bruker ER 200tt instrument, using a solid solution of Mn^{III}-doped (190 p.p.m.) MgO as reference. [b] Splitting constants and line-widths measured in gauss (G; G = 10^{-4} T); symbols for splitting constants as used in ref. 2. [c] Lit. values, see ref. 2, pp. 151 and 156. [d] This refers to polycrystalline $Ag^{II}TPP$ doped into free-based H_2TPP.

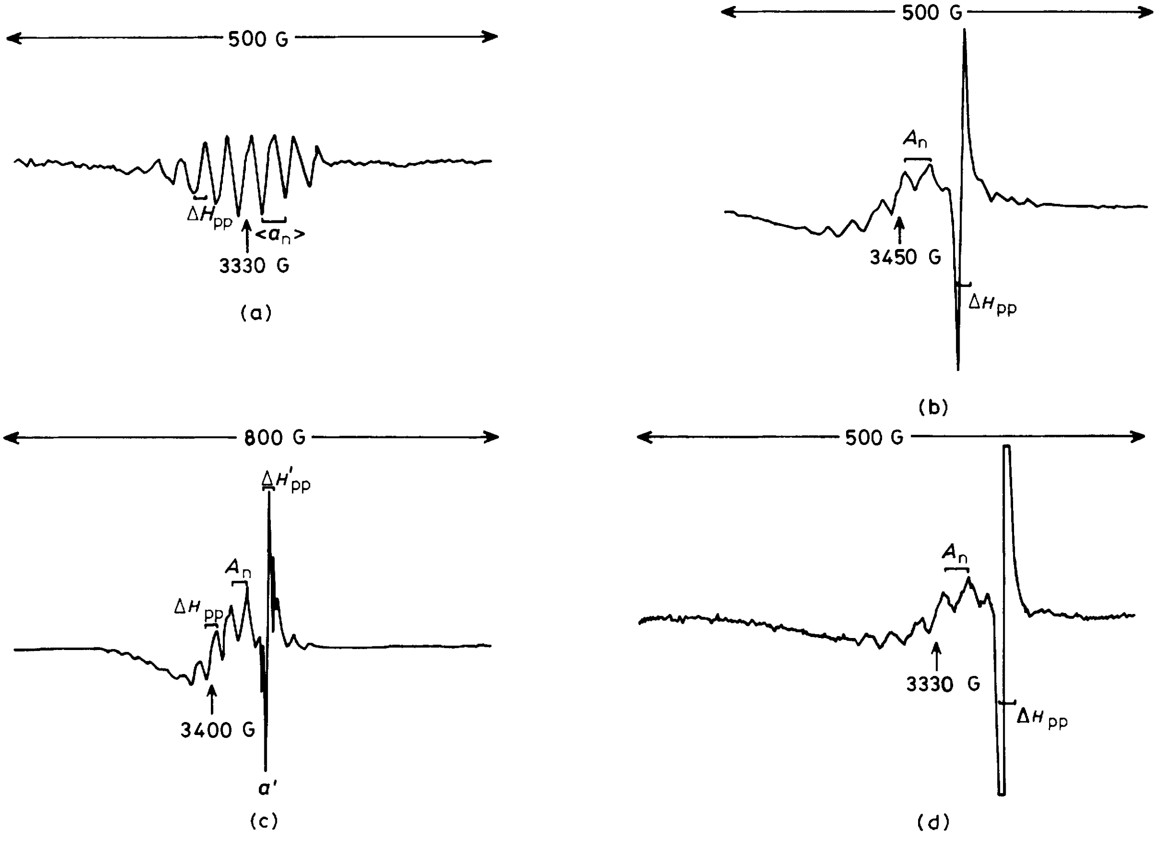
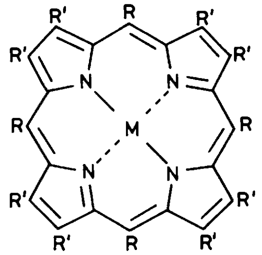


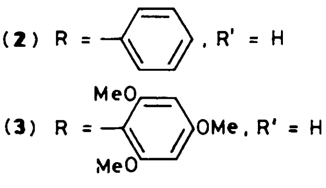
Figure 1. E.s.r. spectra of Ag^{III} metalloporphyrins: (a) (**2a**) and (**3a**) in CH_2Cl_2 and $CHCl_3$ (10^{-1} M), respectively; (b) polycrystalline (**2a**); (c) polycrystalline (**3a**); (d) polycrystalline (**1a**).

macrocycle, leading to $Ag^{II}P^{\cdot+}$ cation radicals, which subsequently decompose back to the Ag^{II} porphyrin. In support of this view, we provide an argument, based on previously observed[8] ^1J (^{13}C–$^1H_{methine}$) n.m.r. coupling constants.

Like that of the dication, H_4OEP^{2+}, the ^1J value for (**1a**)[8] is larger (161 ± 2 Hz) than other diamagnetic metalloporphyrin complexes (152—156 Hz). A previous report on the proton-coupled ^{13}C spectrum of the tropylium cation ascribes its large ^1J value[9] (166 Hz, compared to 156 Hz for cycloheptene) as owing to the presence of delocalised positive charge on the carbocyclic ring. We propose that the central positive charges in H_4OEP^{2+} and on the Ag^{III} cation in (**1a**) can similarly affect the *meso*-carbon ^1J values of the porphyrin ring, either inductively *via* the nitrogen atoms or through the porphyrin π-system. As in other square-planar d^8 metalloporphyrins, the Ag^{III} cation is ideally situated to use its d-orbitals to backbond into the porphyrin π*-system.[6,8] This mechanism would serve to stabilise the build up of electron density on the metal cation (*cf.* low valent metal carbonyls and cyanides, *etc.*). Indeed, *X*-ray photoelectron spectroscopy of (**1a**)[10] confirms a slight increase in electron density over the porphyrin π-system. If this is considered with the known[10] slight reduction in positive



(1) R = H, R' = Et



a; M = Ag^{III}
b; M = Ag^{II}

(For **a**, counterion is ClO_4^-.)

Table 2. DC 4-probe conductivity measurements.

Porphyrin	Conductivity/S cm^{-1}
(1)	$<10^{-8}$
(1a)	1.59×10^{-7}
(1b)	1.00×10^{-7}
(2)	$<10^{-8}$
(2a)	1.50×10^{-7}
(2b)	3.00×10^{-6}
(3)	$<10^{-8}$
(3a)	1.75×10^{-6}
(3b)	5.00×10^{-8}

charge at the Ag^{III} cation, caused by strongly co-ordinated perchlorate anion, then we suggest that these mechanisms may be enough to produce a small equilibrium concentration of Ag^{II}P$^{+\cdot}$ cation radical, which could be reduced back to Ag^{II}P by solution or atmospheric impurities (*cf.* the known decomposition of Ni^{III}TPP$^+$ back to Ni^{II}TPP, *via* the Ni^{II}TPP$^{+\cdot}$ cation radical[11]). The presence of trace amounts of Ag^{II}P in Ag^{III}P samples would therefore account for the broadened n.m.r., the t.l.c., and the e.s.r. activity.

The nature of the Ag^{III}P reductant is at the moment unclear. The water-soluble Ag^{III} metalloporphyrin, *meso*-tetrakis(4-methylpyridyl)porphyrinatosilver(III) is known to be similarly unstable, decomposing back to the Ag^{II} porphyrin on standing in aqueous solution,[4c] or on attempted separation as the perchlorate salt.[4d] Water cannot be the reducing species in this case, as the E° for this Ag^{III}/Ag^{II} couple (0.84 V)[4d] is well below the potentials necessary for water oxidation.

That Ag^{II}P$^{+\cdot}$ is not observed in the dichloromethane solution e.s.r. spectra reported here, may be owing to quenching of the cation radical by dimerisation[12] or by the presence of solvent or atmospheric impurites.[12b] The more intense lines shown in the solid-state e.s.r. spectra (Figure 1) might be due to Ag^{II}P$^{+\cdot}$ cation radicals trapped in the Ag^{III}P matrices, prior to reduction to Ag^{II}P. Indeed, the apparent triplet shown by (**3a**) could be rationalised in terms of unpaired electron density finding its way onto the 2,4,6-trimethoxyphenyl *meso*-substituents. However, the possibility mentioned earlier (of unpaired electron density delocalised over several macrocyclic units) would tend to rule out this interpretation of the extra line, especially if this coincided with raised conductivities compared to typical metalloporphyrins [~10^{-11} S cm^{-1} (ref. 13)]. We have carried out DC 4-probe conductivity measurements on compressed pellets of the Ag^{III} and Ag^{II} metalloporphyrins (Table 2). The data show that the Ag^{III} complexes exhibit modest conductivity four to five orders of magnitude greater than the metal-free and typical metalloporphyrins. Unexpectedly, however, the parent Ag^{II} complexes demonstrate similar conductivities. It must be remembered that the measurements were made on compressed pellets and therefore interparticulate contact resistances may play a significant part in determining the level of conductivity. Any further insight into the role of the Ag^{II}P impurities on the electrical conduction properties of this class of metalloporphyrin must await the growth of single crystals for conductivity measurements and *X*-ray crystal studies.

At the moment, therefore, we are uncertain about the mechanism of conduction, but suggest that electron-rich *meso*-substitutuents [as in (**3a**)] may play an active role. We are working towards improving the conductivities of these systems by (i) changing the *meso*-substituents so that they have greater electron-donating power, and (ii) replacing the perchlorate anion with planar redox-active anions, such as tetracyanoquinodimethane (TCNQ).

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