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Synthesis and spectroscopic studies of manganese porphyrin-thiolate complexes

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Abstract—The synthesis and spectroscopic characterization of four manganese(III) porphyrin thiolates are reported. The investigated compounds are represented by (TPP)Mn(SR), where TPP is the dianion of tetraphenylporhyrin and R is C_6H_5, $C_6H_4(p\text{-}NO_2)$, Et_2NCS and C_4H_8NCS. Each complex was characterized by UV-vis and ^1H NMR spectroscopy. The effects of axial ligands on the UV-vis spectra of synthesized manganese porphyrin complexes is discussed and proton isotropic shifts are shown to be predominantly contact in origin, reflecting extensive porphyrin-to-metal π bonding. © 1997 Elsevier Science Ltd

Keywords: manganese porphyrin thiolate; synthesis; UV-vis; NMR.

Manganese porphyrins have long been studied as model compounds for tetrapyrrole-containing enzymes which are involved in several biological processes [1–4]. More recently they have been used for DNA cleavage [5] and could also be considered as potential contrast enhancement agents for magnetic resonance imaging [6]. The unusual optical properties of Mn^{III} porphyrins and the effects of axial ligation on it have been the center of recent attention [7–9]. The most studied synthetic manganese porphyrins are those with halide or pseudo-halide anions as axial ligands, although compounds with other types of axial ligands have been characterized [10–12]. No studies of manganese porphyrin thiolate compounds have yet appeared in the literature. Recently a number of iron and ruthenium porphyrin thiolates have been synthesized and mimic the physical and spectroscopic properties of the active site of P_{450} at various stages of its catalytic cycle [13–15], for one of the remarkable features of P_{450} as a heme enzyme is that the heme iron has a thiolate(RS^-) coordination [16–17]. In the present paper, we describe the first synthesis and spectroscopic properties of four Mn^{III} porphyrin thiolates, which are represented by (TPP)Mn(SR), where TPP is the dianion of tetraphenylporphyrin and R is C_6H_5, $C_6H_5(p\text{-}NO_2)$, Et_2NCS and C_4H_8NCS. Each complex was characterized by UV-vis and ^1H NMR spectroscopy.

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EXPERIMENTAL

Chemicals

Reagent grade CH_3OH, $CHCl_3$, PhSH, $Et_2NCSSNa$ and $C_4H_8NCSSNa$ were used as received. Tetraphenyl porphyrin(H_2TPP), chloromanganese porphyrin(TPP)MnCl and (p-NO_2) PhSH were prepared by established routes [18–20].

Preparation of the compounds

(TPP)Mn(SPh). To a CH_3OH solution (15 cm^3) of (TPP)MnCl(0.12 g, 0.17 mmol), mercaptide PhSNa(1 cm^3, 2 mmol) solution which was obtained by mixing equal molar PhSH and 2 mol × dm^{-3} NaOH solution was added. Upon stirring for 10 min, a black microcrystalline product appeared. The reaction mixture was continuously stirred for 1 h, the product was collected by filtration, then washed two times with 50 cm^3 50% CH_3OH solution and dried *in vacuo*, giving 0.11 g (83%) of black crystal product. Magnetic susceptibility of (TPP)Mn(SR) was determined as μ_{eff} = 4.71 B.M. at 286 K, which shows that the synthesized complex is in the high spin state (S = 2). Found: C, 76.8; H, 4.2; N, 7.0. Calc. for $C_{50}H_{33}N_4MnS$: C, 77.3; H, 4.3; N, 7.2%.

(TPP)Mn(SPh-p-NO_2). The same method was used with p-NO_2-PhSH, and gave (TPP)Mn(SPh-p-NO_2)

in 78% yield. Found: C, 73.4; H, 3.9; N, 8.3. Calc. for $C_{50}H_{32}N_5O_2MnS$: C, 73.1; H, 3.9; N, 8.5%.

(TPP)Mn(SSCNEt$_2$). To a solution of 0.10 g (0.14 mmol) of (TPP)MnCl in CH_3OH (15 cm^3) was added $Et_2NCSSNa$ (0.06 g, 0.35 mmol), after stirring for 1.5 h at room temperature, a small portion of water (1 cm^3) was slowly added to the solution and then dark crystals appeared. After 30 min, the product was collected and washed with 5% $Et_2NCSSNa$ solution first, then with CH_3OH, and dried *in vacuo*, affording dark crystals (yield 88%). Found: C, 71.9; H, 4.6; N, 8.4. Calc. for $C_{49}H_{38}N_5MnS_2$: C, 72.1; H, 4.7; N, 8.6%.

(TPP)Mn(SSCNC$_4$H$_8$). The same method was used with $C_4H_8NCSSNa$ and gave (TPP)Mn(SSCNC$_4$H$_8$) in 82% yield. Found: C, 72.4; H, 4.3; N, 8.7. Calc. for $C_{49}H_{36}N_5MnS_2$: C, 72.3; H, 4.4; N, 8.6%.

Instruments

Electronic absorption spectra were recorded on a Shimadzu UV-240 spectrophotometer. ^{1}H NMR spectra were recorded at 200 MHz on a Bruker AC-P200 spectrometer. Spectra were measured with 5 mg of the sample in deuterated solvents at room temperature.

RESULTS AND DISCUSSION

Synthesis

The conversion of (TPP)MnCl to (TPP)Mn(SR) proceeds as shown in eq. (1) and was monitored spectroscopically by following the change of UV-vis. The resulting (TPP)Mn(SR) complexes more easily decompose and are reduced than the starting compound (TPP)MnCl. Addition of pyridine or other strong nitrogen base ligand (L) accelerates the reduction of (TPP)Mn(SR) and the divalent porphyrin Mn^{II}(TPP)(L) is obtained as shown in eq. (2). These results are similar to those reported for ferric octaethylporphyrin thiolates [21].

$$(TPP)MnCl + RSNa \longrightarrow (TPP)Mn^{III}(SR) + NaCl \quad (1)$$

$$(TPP)Mn^{III}(SR) + L \longrightarrow (TPP)Mn^{II}(L) + RSSR \quad (2)$$

Spectral properties of (TPP)Mn(SR)

The principal optical absorption features of the (TPP)Mn(SR) complexes and other well known (TPP)Mn(X) (X = Cl, Br, I, F, N_3, SCN) complexes in $CHCl_3$ are given in Table 1. Bands numbered VI, V, IV, III in Table I are in accordance with the terminology of Boucher [1]. The results in Table I show that in the order of the hardness of the axial anions, the position of each band shifts to longer wavelengths with rising ε(III)/ε(IV) and attenuating ε(V)/ε(VI). The pattern of the axial ligand dependence of the ε(III)/ε(IV) ratio suggests that this ratio is particularly sensitive to the hardness of the axial ligand field and the size of the coordinating atom. In fact there appears to be a simple distinction between hard and soft ligands, with ligands having ε(III)/ε(IV) < 1.2 being hard. Apparently the crystal field of a hard axial ligand elevates the metal d_{z^2} orbital and so restricts porphyrin σ donation into this orbital.

The anion dependence of the intensity of the absorption maxima may be related to metal–porphyrin π mixing. Hard acid anions stabilize a high positive charge on the metal atom with the resulting high charge in the porphyrin. In this case, π bonding should be strong and the charge-transfer bands are intense. Conversely, with soft anions, the intensity of the charge-transfer bands is low. The intensity changes when going from the fluoride to the thiolate complexes

Table 1. Room temperature spectral properties for Mn(TPP)(X) at about 10^{-5} mol × dm^{-3} in CH_2Cl_2

X$^-$	Band VI λ(nm)	Band V λ(nm)	Band IV λ(nm)	Band III λ(nm)	ε(III)/ε(IV)	ε(V)/ε(VI)
F^-	366	457	572	606	0.82	4.16
NO_3^-	387	480	575	609	0.88	1.22
$CH_3CO_2^-$	372	470	577	612	0.96	2.58
NO_2^-	381	477	580	615	1.03	1.69
Cl^-	375	478	582	619	1.18	1.93
Br^-	380	485	588	626	1.32	1.33
N_3^-	382	486	590	628	1.45	1.00
CN^-	387	495	600[a]	640	1.61	1.04
I^-	388	498	598[a]	634	1.69	0.65
Et_2NCSS^-	388	501	609[a]	650	1.72	0.43
$C_4H_8NCSS^-$	392	503	610	655	1.52	0.50
NO_2PhS^-	390	505	613	665	1.26	0.30
PhS^-	395	500	613	675	1.57	0.34

[a]Unresolved shoulder.

are consistent with this proposal. The anion dependence of the energy and intensity of the absorption maxima may also be due to differences in coordination geometry. With small axial anions like fluoride, the metal may be in the plane of the porphyrin. Conversely, with large anions like iodide and thiolate compounds, the metal may be considerably out of plane and other anions complexes would fall between the two extremes. In the planar case, back π bonding would be strong and the charge transfer bands intense. Another consequence of this would be a high negative charge in the porphyrin and blue shifted absorption bands. In the out-of-plane case, back π bonding would be weaker and the charge transfer bands relatively less intense. Hence, a red-shifted spectrum would be observed.

^{1}H NMR data of the synthesized compounds are summarized in Table 2. The chemical shifts and the line-widths (18–860 Hz) are characteristic of paramagnetic compounds and assignment of the (TPP)Mn(SR) resonances can be made by comparison with previously characterized manganese(III) porphyrins containing other axial ligands such as Cl^-, ClO_4^- or N_3^- [22, 23]. The pyrrole-H signals of the TPP complexes appear as the broadest peaks (840 Hz) in the ^{1}H NMR spectra and are located at *ca* -22.7 and -25.6 ppm. Resonances for the *m*-H and *p*-H protons are seen at *ca* 8.3 and 7.5 ppm respectively, but none of the *o*-H resonances are detected. The proton resonance of the axial ligand usually has a large up or down field shift with a broad line-width (180 ~ 636 Hz). The proton NMR trace of (TPP)Mn(SPh) in $CDCl_3$ is shown in Fig. 1, the two broad up field peaks (-53.1 ppm, -45.2 ppm) and one broad down field peak (33.7 ppm) clearly indicate the presence of C_6H_5S in the axial position of manganese porphyrin.

The isotopic shifts for assigned resonances, referenced against the analogous diamagnetic Zn^{II} complex [23], are listed in Table 3. The observed shifts in Table 3 do not reflect the attenuation of shifts of the same sign, but rather exhibit alternation of sign around the pyrr-H and phenyl rings. This alternating upfield-downfield-upfield shift pattern for the (TPP)Mn(SR) is indicative of TPP^{2-} hydrogen resonances of a contact interaction *via* a π spin delocalization mechanism, since the predicted dipolar shift directions are the same for all positions [24]. LaMar and Walker [25] have demonstrated that the minimal magnetic anisotropy and small zero-field splitting of

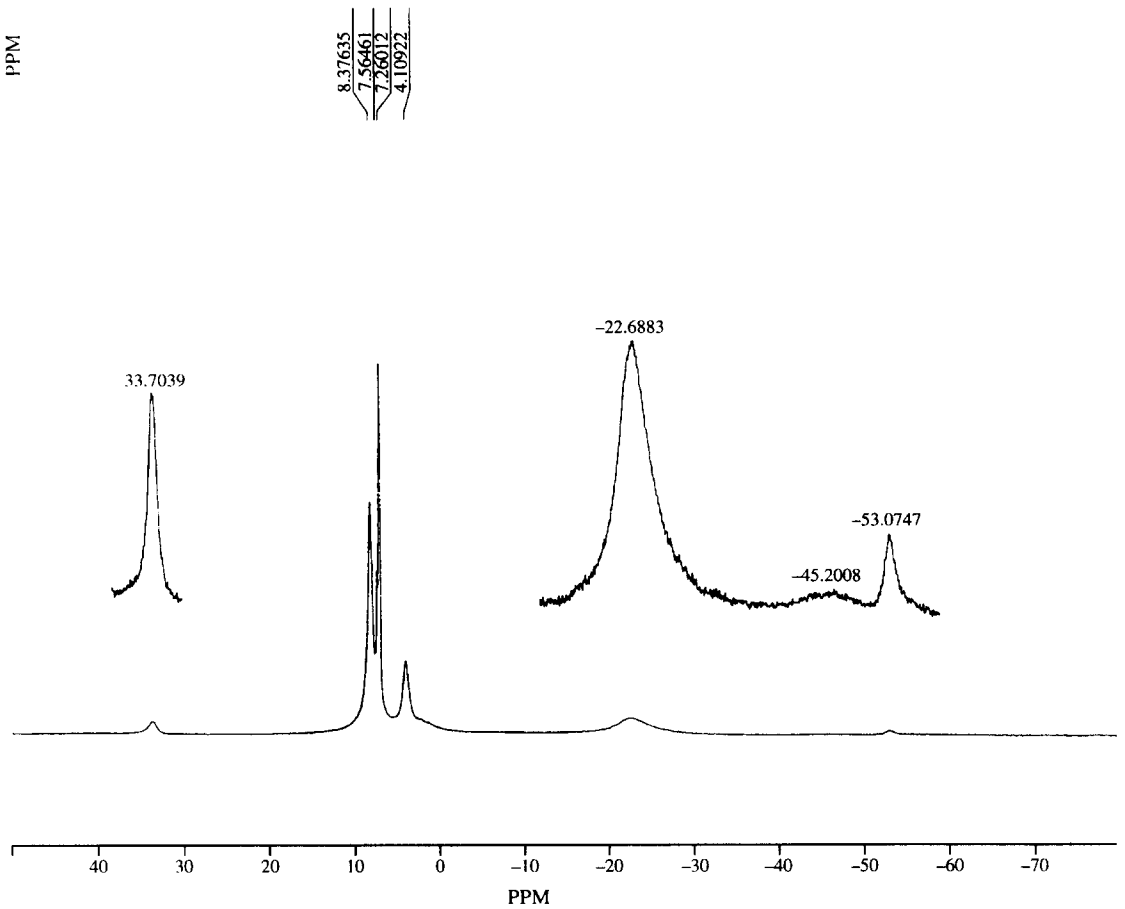

Fig. 1. ^{1}H NMR spectrum of (TPP)Mn(SPh) ($CDCl_3$, 200 MHz, 293 K, shifts in ppm).

Table 2. ^{1}H NMR spectral data of (TPP)Mn(SR) complexes ($CDCl_3$, 200 MHz)[a]

R	β-pyrrole H_β	Phenyl $H_0^b + H_m + H_p$	Axial ligand
Ph	−22.7(br,8H)	8.4,7.5(d,20H)	−53.1(br,1H,H_p'), −45.2(br, 2H,H_0'),33.7(br,2H,H_m')
C_4H_8NCS	−25.3(br,8H)	8.3,7.2(d,20H)	63.5(br,8H)
Et_2NCS	−25.2(br,8H)	8.3,7.3(d,20H)	32.3(br,10H)
Ph-*p*-NO_2	−25.6(br,8H)	8.3,7.2(d,20H)	33.1(br,2H,H_m'),[b]H_0'

[a]At 293 K, shift in ppm.
[b]Unresolved.

Table 3. Observed isotopic shifts of (TPP)Mn(SR)[a]

R	Pyrrole-H	m-H	p-H
Ph	31.54	−0.60	0.23
(*p*-NO_2)Ph	34.45	−0.56	0.51
C_4H_8NCS	33.85	−0.57	0.51
Et_2NCS	33.85	−0.59	0.51

[a]Shifts in ppm, against dimagnetic Zn(TPP).

a porphyrin coordinated manganese(III) ion ensures that the isotope shifts and resonance broadening in the proton NMR spectrum arise almost entirely from "through bond" contact interaction *via* a π spin delocalization mechanism.

The values for the isotropic shifts of pyrr-H of (TPP)Mn(SR) increase upfield in the order $C_6H_5 < C_4H_8NCS \approx Et_2NCS < C_6H_4$-*p*-$NO_2$. The increase in the pyrr-H contact shift must therefore be an increase in P → Mn π charge transfer. It seems reasonable to assume that changes in Mn—P π bonding result from changes in Mn—SR π bonding. In terms of π bonding, SR can only act as a donor, in the order $C_6H_5 > C_4H_8NCS \approx Et_2NCS > C_6H_4$-*p*-$NO_2$. Hence, the change in pyrr-H contact shift reflects the competition between SR and P as donor, as the π donor of strength of SR decrease, the extent of P → Mn π charge transfer increases.

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