

# Unusual transformations of a manganese(III) porphyrin

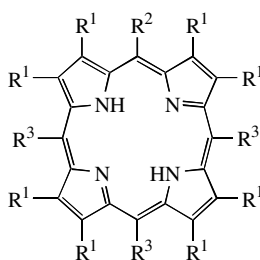
Maria E. Klyueva\* and Tatyana N. Lomova

Institute of Solution Chemistry, Russian Academy of Sciences, 153045 Ivanovo, Russian Federation.  
Fax: +7 0932 37 8509; e-mail: mek@ihnr.polytech.ivanovo.su

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A superstable SAT (sitting atop) complex was synthesised by the incomplete dissociation of a chelate of manganese(III) with *meso*-monophenyl-octamethylporphine in a solid state.

Functional substitution at different positions of porphyrin molecules strongly influences their properties. The manganese(III) complex (Cl)MnP with *meso*-monophenyl-octamethylporphine **1** was synthesised by a usual coordination reaction in DMF.<sup>1</sup> The product was extracted with CHCl<sub>3</sub>, washed and purified by preparative chromatography on Al<sub>2</sub>O<sub>3</sub> using CHCl<sub>3</sub> with 2% EtOH.

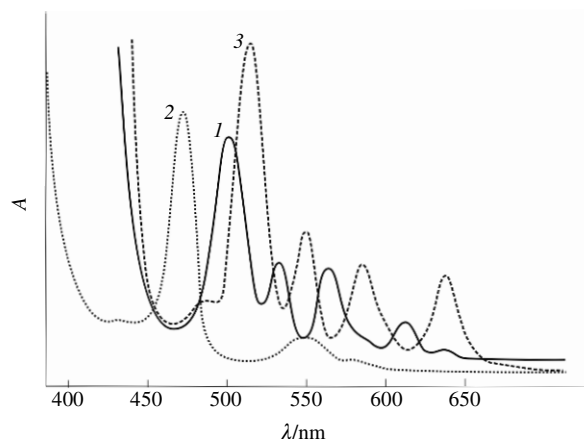
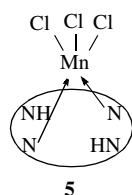


- 1 R<sup>1</sup> = Me, R<sup>2</sup> = Ph, R<sup>3</sup> = H
- 2 R<sup>1</sup> = Et, R<sup>2</sup> = Ph, R<sup>3</sup> = H
- 3 R<sup>1</sup> = Et, R<sup>2</sup> = R<sup>3</sup> = H
- 4 R<sup>1</sup> = H, R<sup>2</sup> = R<sup>3</sup> = Ph

The UV-VIS spectra of porphyrin **1** and (Cl)MnP are shown in Figure 1 (curves 1 and 2). After chromatographic purification, concentrated hydrochloric acid was added to the (Cl)MnP solution (1×10<sup>-4</sup> mol dm<sup>-3</sup>) to achieve an acid concentration of 2×10<sup>-4</sup> mol dm<sup>-3</sup>. Then, the solvent was evaporated. The solid residue was kept in air for five days, dissolved in CHCl<sub>3</sub> pre-treated with an ammonia solution, washed with water and purified on Al<sub>2</sub>O<sub>3</sub> with CHCl<sub>3</sub>. Four intense bands are observed in the visible region of the absorption spectrum of the product, which are bathochromically shifted as compared with those of **1** (curve 3 in Figure 1). In porphyrins **2–4**, such transformations do not occur. The product was identified by TLC, R<sub>f</sub> = 0.50 (benzene:hexane, 1:2, Silufol). According to atomic absorption analysis, the product is diamine-type porphyrin complex **5** or the SAT complex [Mn(Cl)<sub>3</sub>H<sub>2</sub>P], where two pyrroline nitrogens are coordinated to the metal ion and two protons remain on the pyrrole nitrogens. Manganese contents: found, 8.40%; calculated, 8.32%.

The way of SAT complex formation by incomplete dissociation of chelates in a solid state is novel. Indeed, the formation of the SAT complex was considered as one of the two possible routes of interaction of porphyrin with a metal salt in a solution<sup>2–6</sup> or a limiting step of porphyrin interaction with a metal salt yielding the chelate compound MP in non-polar media.<sup>7–11</sup> The covalent complexes of porphyrin dianions with almost all metals were synthesised and characterised, whereas the possibility of formation, the structure and properties of the corresponding SAT complexes were inadequately studied.

The <sup>1</sup>H NMR spectrum of SAT complex **5** differs from that of paramagnetic manganese(III) porphyrin. The Mn<sup>3+</sup> cation in **5** does not have a strong disturbing influence on the macrocyclic



**Figure 1** Electronic absorption spectra in CHCl<sub>3</sub> (λ<sub>max</sub>/lg ε): (1) monophenyl-octamethylporphine (**1**), (2) (chlorine)manganese(III)monophenyl-octamethylporphine (Cl)MnP, and (3) the SAT complex of manganese with **1** [Mn(Cl)<sub>3</sub>H<sub>2</sub>P].

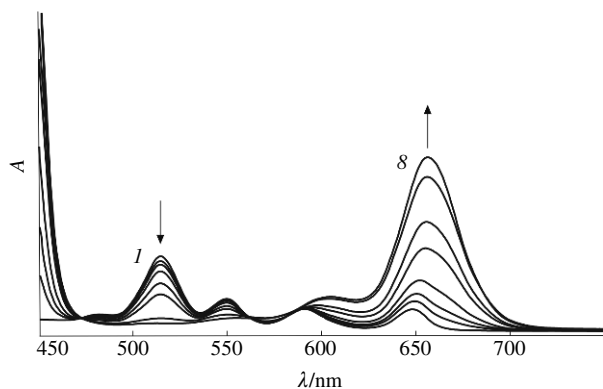
ring, as compared with the metal porphyrin. In the <sup>1</sup>H NMR spectrum of the SAT complex in CDCl<sub>3</sub> (Bruker 200 MHz; HMDS as an internal standard), the well resolved signals of NH protons [δ -2.79 (s)], *meso*-protons [8.84 (s)], Me groups at the β-positions of the macrocycle [1.56 (s), 1.25 (s), 0.86 (s)] and *o*-, *m*- and *p*-phenyl protons [8.22 (m), 7.75 (m)] are observed. Exocyclic *meso* and β-Me protons in SAT complex spectrum are significantly upfield shifted as compared with those for **1**, whereas NH-proton signals are downfield shifted. These changes are evidence for a decrease in macrocyclic ring current intensity as a result of SAT complex formation, i.e., of a decrease in the aromaticity of the compound.

Changes in the spectral characteristics (UV-VIS and <sup>1</sup>H NMR) observed after SAT complex formation, as compared with porphyrin **1**, are analogous to those described by Funahashi *et al.*<sup>7,8,11</sup> for transition metals. In the cited works, the structure of the SAT complexes in solutions was confirmed by the fluorescent EXAFS method for a Cu complex with teraphenylporphyrin.

We synthesised the first SAT complex of an asymmetrical *meso*-substituted porphyrin, which is very stable in a solid state and in solutions. The addition of an acid to SAT complex solutions in CHCl<sub>3</sub>, DMF and C<sub>6</sub>H<sub>6</sub> results in a new form of the complex with one intense band at 648–658 nm (depending on the acid and its concentration) in the electronic absorption spectrum. It differs from the spectrum of compound **1** in acid-containing solutions (λ<sub>max</sub> 558 nm). Figure 2 shows changes in the electronic absorption spectrum on the titration of the SAT complex solution in CHCl<sub>3</sub> with glacial acetic acid. The equilibrium constant K = (0.7±0.2) dm<sup>6</sup> mol<sup>-2</sup> at 298 K. The SAT complex dication [Mn(Cl)<sub>3</sub>H<sub>4</sub>P]<sup>2+</sup>[AcO<sup>-</sup>]<sub>2</sub> (curve 8 in Figure 2) is the product of equilibrium (1).



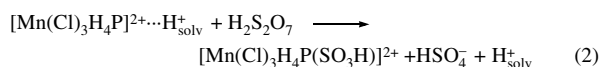
The formation of the dication is reflected in the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub> + 0.5% CF<sub>3</sub>COOH). The NH-proton signal is strongly (> 3 ppm) upfield shifted and appears at 0.39 ppm, its integral intensity is doubled. The *meso*-proton signal is upfield



**Figure 2** Changes in the electronic absorption spectra of the SAT complex during titration of its chloroform solution with glacial acetic acid.  $C_{\text{AcOH}}^0 / \text{mol dm}^{-3}$ : (1) 0, (8) 5.11; other curves correspond to intermediate AcOH concentrations.

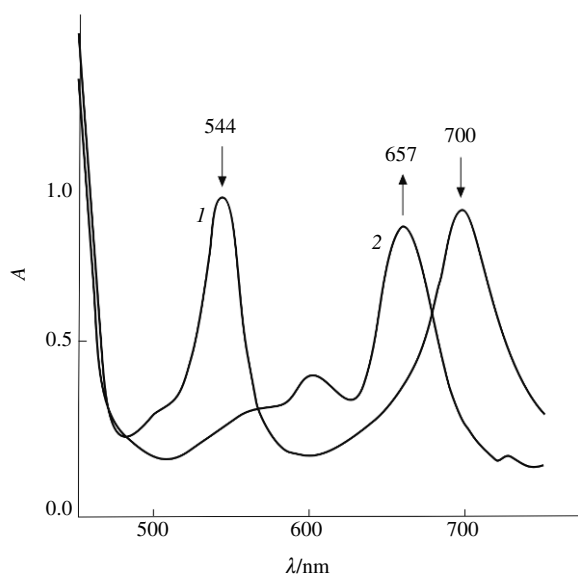
shifted (8.60 ppm). The positions of the signals of Me protons remained almost unchanged, an *o*-, *m*- and *p*-phenyl protons give a multiple signal at 7.99 ppm. The spectrum shows a further decrease in the macrocyclic-ring current and aromaticity of the compound.

In concentrated sulfuric acid solutions, the protonation of the SAT complex takes place, and a new form is identified by a characteristic electronic absorption spectrum with wide intense bands at 542 and 694 nm (Figure 3, curve 1). A similar spectrum was observed earlier for H-associates of metal porphyrins and the tetraphenylporphine dication in solutions with high proton concentration.<sup>12</sup> Thus, in our case, the associate  $[\text{Mn}(\text{Cl})_3\text{H}_4\text{P}]^{2+} \cdots \text{H}_{\text{solv}}^+$  is formed. The heating of the sulfuric acid solutions results in the transfer of the visible spectrum of the compound to the spectrum of the SAT complex dication with a sulfurised phenyl ring,  $\lambda_{\text{max}} = 657 \text{ nm}$  (Figure 3). Reaction (2) is described by third-order rate equation (3).



$$-dC_{[\text{Mn}(\text{Cl})_3\text{H}_4\text{P}]^{2+} \cdots \text{H}_{\text{solv}}^+} / d\tau = C_{[\text{Mn}(\text{Cl})_3\text{H}_4\text{P}]^{2+} \cdots \text{H}_{\text{solv}}^+} C_{\text{H}_2\text{S}_2\text{O}_7}^2 \quad (3)$$

where  $C_{\text{H}_2\text{SO}_4}$  is the equilibrium concentration of unionised  $\text{H}_2\text{SO}_4$  molecules in concentrated sulfuric acid calculated using the Brand equation<sup>13</sup> as described previously.<sup>12</sup> The rate constant of reaction (2) at 298 K is  $k^{298} = (18.0 \pm 0.7) \times 10^{-9} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ , the activation energy is  $E = (88.5 \pm 0.5) \text{ kJ mol}^{-1}$  and the activation entropy is  $\Delta S^\ddagger = (-103 \pm 2) \text{ J mol}^{-1} \text{ K}^{-1}$ .



**Figure 3** Electronic absorption spectra of the SAT complex (1) in 17.5 M  $\text{H}_2\text{SO}_4$  at 298 K and (2) after heating the solution to 353 K for 2 h.

Manganese(III) porphyrin was isolated as a result of recrystallization of the product of reaction (2) from concentrated  $\text{H}_2\text{SO}_4$  by pouring the solution onto ice. It exhibits visible bands shifted hypsochromically by 3–4 nm as compared with the bands in the spectrum of (Cl)MnP because the phenyl ring of the compound is sulfurised.

The SAT complex structure was confirmed by the optimization of the geometrical structure of the compound by the quantum-chemical semi-empirical method CINDO1. A given gradient of  $0.04 \text{ kJ mol}^{-1} \text{ \AA}^{-1}$  was the condition of ending the calculations.

Thus, the combination of one electron-withdrawing phenyl group and eight electron-donor methyl groups as functional substituents in the porphyrin structure leads to the appearance of the unique ability of the compound to form a very stable SAT complex having a significant basicity in the molecular state.

## References

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