

Transmetallation of a Manganese(II)-porphyrin by Zn²⁺ Ions in the Presence of Thiols

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Manganese(II)-tetraphenylsulphonatoporphyrin (tpps) undergoes transmetallation by Zn²⁺ ions in the presence of thiol compounds, a thiol-ligated metalloporphyrin, [RS-Mn^{II}-(tpps)]⁵⁻, being the active species.

Metalloporphyrins are essential ingredients in a variety of biological systems, *i.e.* hemoglobin, cytochromes, *etc.*^{1,2} Furthermore, various metalloporphyrins appear in oils and sediments.³ Thus, there is substantial interest in the investigation of metallation processes of porphyrins as well as the transmetallation of metalloporphyrins as models for biochemical and geochemical transformations.⁴ We report here the transmetallation of manganese(II)-*meso*-tetraphenylsulphonatoporphyrin, [Mn^{II}-(tpps)]⁴⁻, by Zn²⁺ ions in aqueous solutions at ambient temperature. This process occurs only in the presence of thiols, RSH, which assist the transmetallation process, *via* co-ordination to the manganese(II)-porphyrin.

Addition of Zn²⁺ ions to an aqueous solution of [Mn^{III}-(tpps)]⁴⁻ does not yield any transmetallation product. Reduction of [Mn^{III}-(tpps)]⁴⁻ by H₂ (in the presence of PtO₂) yields [Mn^{II}-(tpps)]⁴⁻ (λ_{max} , 432 nm).^{5,6} Addition of Zn²⁺ ions to [Mn^{II}-(tpps)]⁴⁻ also does not effect any transmetallation process. However, addition of ethanethiol (1.6×10^{-2} M) or cysteine (1.6×10^{-2} M) to an aqueous solution of [Mn^{III}-(tpps)]⁴⁻ (7×10^{-6} M) results in the reduction of [Mn^{III}-(tpps)]⁴⁻ to [Mn^{II}-(tpps)]⁴⁻. Subsequent addition of Zn²⁺ ions leads to the formation of the transmetallated product, zinc(II)-*meso*-tetraphenylsulphonatoporphyrin [Zn^{II}-(tpps)]⁴⁻ (Figure 1). Also, [Mn^{II}-(tpps)]⁴⁻, prepared by H₂/PtO₂ reduction, undergoes transmetallation with Zn²⁺ in the presence of cysteine or ethanethiol. Thus, it is evident that [Mn^{II}-(tpps)]⁴⁻ undergoes transmetallation by Zn²⁺ in the presence of thiols, while in their absence this process is prevented.

To account for this behaviour, we have examined the effect of added thiols on the visible absorption spectrum of

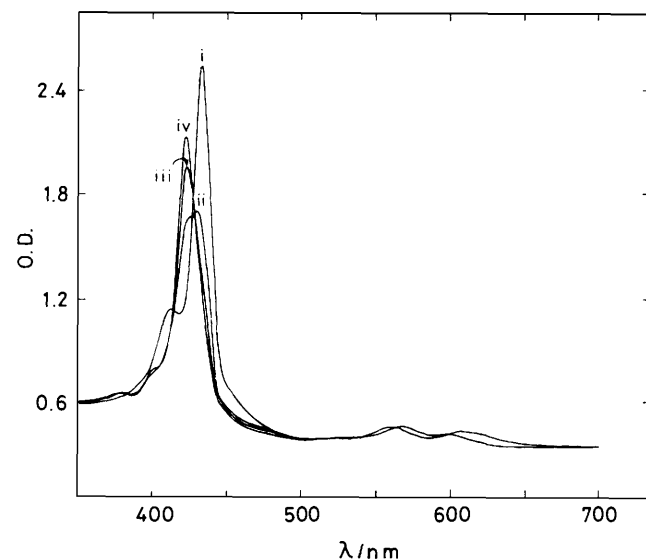
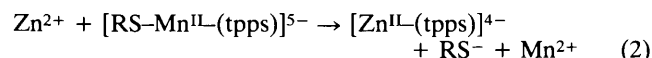
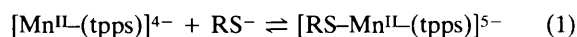


Figure 1. Transmetallation of [RS-Mn^{II}-(tpps)] by Zn²⁺, 2.33×10^{-3} M, in the presence of ethanethiol, 1.6×10^{-2} M; (i) before the addition of Zn²⁺; (ii) 2 min after addition; (iii) 4 min after addition; (iv) 6 min after addition.

[Mn^{II}-(tpps)]⁴⁻ produced by reduction with H₂/PtO₂ (Figure 2). Addition of increasing amounts of ethanethiol results in the decrease of the absorption band of [Mn^{II}-(tpps)]⁴⁻ at 432 nm and the concomitant formation of a new absorption band at 412 nm. Two isosbestic points are observed upon increasing the amount of added thiol. Upon addition of O₂ the absorption bands at 432 and 412 nm both disappear and [Mn^{III}-(tpps)]⁴⁻ is formed quantitatively. All these results imply that a 1:1 complex of [Mn^{II}-(tpps)]⁴⁻ with the thiol is formed [equation (1)]. Similar thiol group ligation to other metalloporphyrins, *i.e.* Co^{III}-porphyrins, has been described previously.⁷ The association constants of these complexes with ethanethiol and cysteine are summarized in Table 1.



Addition of Zn²⁺ ions to the complex [RS-Mn^{II}-(tpps)]⁵⁻ results in transmetallation and formation of [Zn^{II}-(tpps)]⁴⁻. Thus, it is evident that the association of thiol ligands with [Mn^{II}-(tpps)]⁴⁻ activates the metalloporphyrin towards the transmetallation reaction (2). This activation might be attributed to the deformation of the complex so that the central Mn^{II} ion lies out of the plane of the porphyrin ligand, resulting in a ligand which is susceptible to transmetallation. The pseudo-first-order rate constants for the reduction of [Mn^{III}-(tpps)]⁴⁻ by ethanethiol and cysteine as well as the rate constants for the transmetallation of the different complexes by Zn²⁺ are also summarized in Table 1.

In conclusion, we have demonstrated that [Mn^{III}-(tpps)]⁴⁻ is reduced by thiols, and a complex, [RS-Mn^{II}-(tpps)]⁵⁻, is

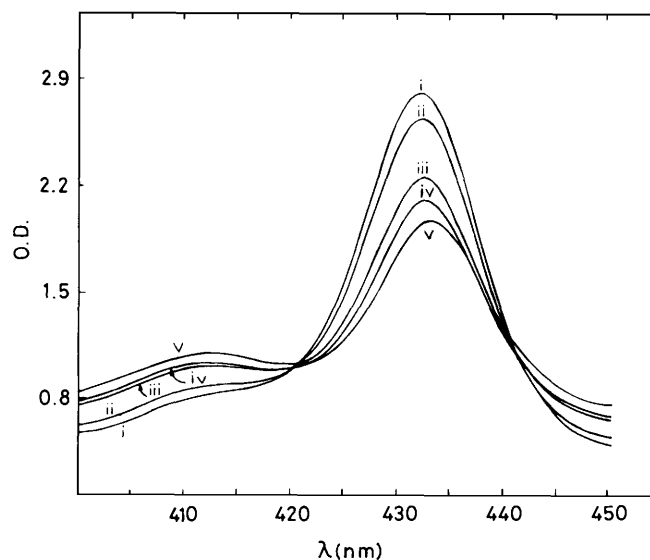


Figure 2. Spectral changes upon addition of ethanethiol to [Mn^{II}-(tpps)]: (i) 7.81×10^{-2} M; (ii) 2.34×10^{-1} M; (iii) 4.68×10^{-1} M; (iv) 7.81×10^{-1} M; (v) 1.17 M.

Table 1. Association and kinetic data for the metalloporphyrins.

Thiol	$K_a^a/$ $\text{dm}^3 \text{mol}^{-1}$	$k_{\text{red.}}^{b,c}/$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$k_{\text{met.}}^{d,e}/$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
HSCH ₂ CH ₂ OH	2.87	1.35×10^{-4}	70.4
HSCH(NH ₂)- CO ₂ H	84.68	2.33×10^{-3}	16.97×10^{-2}

^a Association constant, equation (1), $K_a = [\text{RS-Mn}^{\text{II}}(\text{tpps})]/[\text{Mn}^{\text{II}}(\text{tpps})][\text{RS}^-]$, calculated using the Benesi-Hildebrand equation.⁸

^b Rate constant for reduction of $[\text{Mn}^{\text{III}}(\text{tpps})]^{4-}$ to $[\text{Mn}^{\text{II}}(\text{tpps})]^{4-}$ by the thiols. ^c Determined at 24 ± 2 °C, $[\text{Mn}^{\text{III}}(\text{tpps})] = 7 \times 10^{-6} \text{ M}$, $[\text{RS}^-] = 1.6 \times 10^{-2} \text{ M}$, $[\text{Zn}^{2+}] = 2.33 \times 10^{-3} \text{ M}$. ^d Rate constant for transmetallation of $[\text{RS-Mn}^{\text{II}}(\text{tpps})]^{5-}$ by Zn^{2+} .

formed. The thiol-ligated manganese(II)-porphyrin undergoes transmetallation by Zn^{2+} . Other metal ions, e.g. Fe^{2+} and Ni^{2+} , do not transmetallate the activated complex $[\text{RS-Mn}^{\text{II}}(\text{tpps})]^{5-}$, presumably since they form a complex with the thiols. Thus, selectivity in transmetallation is accomplished. These observations might offer a model for the selective

and specific formation of metalloporphyrins in natural environments or geochemical sediments since thiol compounds are abundant materials in these environments.

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