

# Super-stable metallotetraphenylporphyrins

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Super-stable porphyrin complexes [germanium(IV) and tin(IV)tetraphenylporphyrins], precipitated from concentrated sulfuric acid poured onto ice, have been discovered, together with stable metallophthalocyanines, and their stability is characterised and the dissociation mechanism in proton donor solvents investigated.

It is known that stable metallophthalocyanines crystallize out when their sulfuric acid solutions are poured onto ice. This is used as a method of high purification from admixtures after template synthesis of the complexes.<sup>1</sup> Metalloporphyrins with composition MP (P = porphyrin dianion, M = doubly-charged metal cation) are less stable<sup>2-4</sup> and undergo destruction, being dissolved in concentrated H<sub>2</sub>SO<sub>4</sub>. Before any detailed investigations into the stability of acidoporphyrin complexes of highly charged metal cations of composition (X)<sub>n-2</sub>MP (X = single-charged acido ligand) appeared it had been assumed<sup>5</sup> that all metalloporphyrins were unstable in sulfuric acid. It was shown<sup>6-8</sup> that complexes of tetraphenylporphyrin (X)<sub>n-2</sub>MTTP and O=VOEP with covalent bonding acidoligands X in the first coordination sphere and in some cases complexes with composition MP do not undergo destruction in concentrated H<sub>2</sub>SO<sub>4</sub>. However, it was difficult to identify the complexes in the sulfuric acid solution because they form an H-associate (X)<sub>n-2</sub>MTTP...H<sup>+</sup><sub>Solv</sub> with an electronic absorption spectrum possessing two wide bands at 540 and 700 nm; this differs from the usual spectra of the metalloporphyrin solutions. This applies to (X)MnTPP, (X)FeTPP, O=TiTPP, (Cl)InTPP, (AcO)GaTPP and several of their functional derivatives. Now a qualitative reaction which shows the dissociation process of metalloporphyrins in H<sub>2</sub>SO<sub>4</sub> or its absence has been found.<sup>9</sup> An attempt to crystallize metalloporphyrin bonding into the H-associate leads to dissociation of the complex in all cases.

In this communication new quantitative data about the existence of metalloporphyrins, which are stable in hot (398 K) concentrated sulfuric acid in the molecular form (in contrast to the H-associate), and which can be recrystallized from sulfuric acid solutions similar to stable metallophthalocyanines, are presented. These are (dichlorine)germaniumtetraphenylporphyrin (Cl)<sub>2</sub>GeTPP and (dichlorine)tintetraphenylporphyrin (Cl)<sub>2</sub>SnTPP.

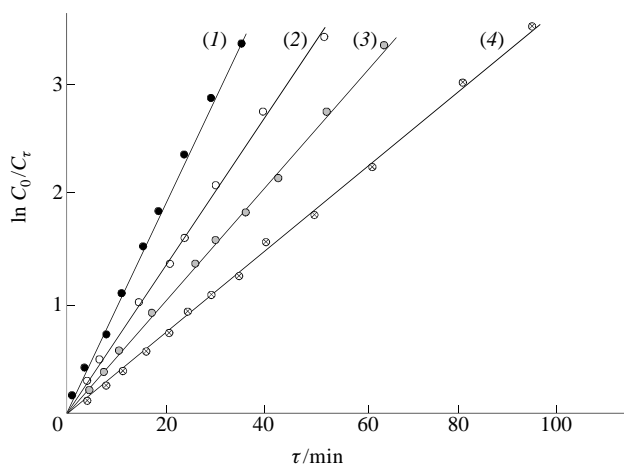
(Cl)<sub>2</sub>GeTPP was obtained as described in ref. 10 by reaction of the complex formation of H<sub>2</sub>TPP with GeCl<sub>4</sub> in quinoline at 510 K under a nitrogen atmosphere. (Cl)<sub>2</sub>SnTPP was obtained

as described in ref. 11 by an analogous reaction of H<sub>2</sub>TPP with SnCl<sub>2</sub> in boiling dimethylformamide. The tin complex was purified by chromatography on an Al<sub>2</sub>O<sub>3</sub> column using CHCl<sub>3</sub> and the germanium complex using CHCl<sub>3</sub> and then diethyl ether. UV/VIS spectra of the complexes coincide with literature data<sup>12,13</sup> λ<sub>max</sub>/nm (lg ε): 402 (sh.), 423 (5.76), 485 (sh.), 516 (3.49), 554 (4.29), 592 (3.83) and 406 (4.63), 428 (5.83), 490 (sh.), 522 (3.56), 561 (4.34), 601 (4.13) for germanium and tin complexes in CHCl<sub>3</sub>, respectively. The complexes are partially dissolved in concentrated H<sub>2</sub>SO<sub>4</sub>, in which their solutions are rose in colour in contrast to the brown solution in case of the H-associate formation. The general character of their visible spectra in sulfuric acid is the same as in organic solvents, but the absorption maxima have lower wavelengths λ<sub>max</sub>/nm: 516, 545, 572 and 510, 547, 586 for the germanium and tin complexes, respectively. After reprecipitation of the germanium and tin complexes from sulfuric acid onto ice their spectra do not change.

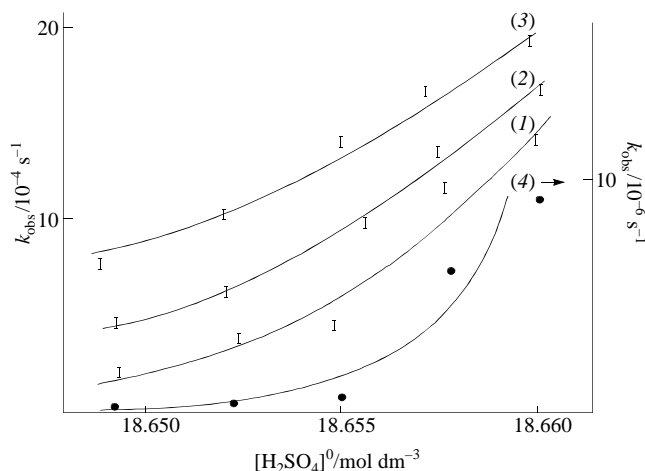
(Cl)<sub>2</sub>MTTP undergoes dissociation [reaction (1)] at a spectrophotometrically measured rate only in media with a maximum proton donor particles content: in H<sub>2</sub>SO<sub>4</sub> at a concentration near 100% over 340 K. In 83–97% sulfuric acid where stable metallophthalocyanines dissociate slowly the tetraphenylporphyrin complexes with Sn and Ge remain unchanged for a long time. This defines the metalloporphyrins as complexes with unsurpassed kinetic stability in solution.



Solvent H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O with acid content 99.94–99.98% was prepared by the weight method from 100% H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> with definite concentration. Experimental constants of the dissociation rate *k*<sub>obs</sub> were defined from dependences ln C<sub>0</sub>/C<sub>τ</sub>–τ (Figure 1) using the least-squares method. Selection of pairs of values of argument and function was 10–12. Each experiment was repeated 2–3 times. Constants for the reaction of (Cl)<sub>2</sub>SnTPP in 100% H<sub>2</sub>SO<sub>4</sub> and (Cl)<sub>2</sub>GeTPP in 99.93–100%



**Figure 1** Dependence of the logarithm of the ratio of initial and current concentrations of metalloporphyrin ln C<sub>0</sub>/C<sub>τ</sub> vs. time τ. C<sub>H<sub>2</sub>SO<sub>4</sub></sub> (%): (1), (3) 99.96; (2), (4) 99.94. T/K: (1), (2) 362; (3), (4) 358.



**Figure 2** Dependence of the observed rate constant for dissociation of (Cl)<sub>2</sub>SnTPP vs. H<sub>2</sub>SO<sub>4</sub> concentration. T/K: (1) 353, (2) 358, (3) 362, (4) 298.

H<sub>2</sub>SO<sub>4</sub> were published earlier,<sup>5,14</sup> and values of  $k_{\text{obs}}$  for dissociation of the tin complex in H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O mixtures were obtained for the first time (Figures 2, 3). It follows from Figure 1 that the rate equation for reaction (1) for the complexes of tin(IV) and germanium(IV) can be expressed by equation (2):

$$-dC_{(\text{Cl})_2\text{MTPP}}/d\tau = k_{\text{obs}}[(\text{Cl})_2\text{MTPP}] \quad (2)$$

However, the influence of the H<sub>2</sub>SO<sub>4</sub> concentration complicates the rate equation. As shown in Figure 2, the plot of the observed rate constant for the dissociation of (Cl)<sub>2</sub>SnTPP vs. [H<sub>2</sub>SO<sub>4</sub>] yields a curve concave to the axis of the rate constant and passing through the origin (the complex does not undergo dissociation in aqueous solutions). A general rate law conforming to this situation is given by equations (3) or (4):

$$k_{\text{obs}} = k_1[\text{H}_2\text{SO}_4]^2 + k_2[\text{H}_2\text{SO}_4] \quad (3)$$

$$k_{\text{obs}}/[\text{H}_2\text{SO}_4] = k_1[\text{H}_2\text{SO}_4] + k_2 \quad (4)$$

The values of  $k_1$  and  $k_2$  obtained from the linear dependence of  $k_{\text{obs}}/[\text{H}_2\text{SO}_4]$  vs. [H<sub>2</sub>SO<sub>4</sub>] [correlation coefficient  $r = 0.97$ ; selection of pairs of values of argument and function (2–3) × 5] within the least-squares method are  $(5 \pm 1) \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  and  $(1.0 \pm 0.2) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively, at 353–362 K. The temperature dependence of the rate constants is within the limits of stated error. An attempt to find the linear correlation of  $k_{\text{obs}}$  and [H<sub>3</sub>O<sup>+</sup>], [H<sub>3</sub>O<sup>+</sup>]<sup>2</sup>, [H<sub>2</sub>SO<sub>4</sub>] or [H<sub>2</sub>SO<sub>4</sub>]<sup>2</sup> leads to worse correlation coefficients. The general rate equation (5) testifies that the dissociation reaction of the tin complex proceeds along two parallel routes.

$$-dC_{(\text{Cl})_2\text{SnTPP}}/d\tau = [(\text{Cl})_2\text{SnTPP}](k_1[\text{H}_2\text{SO}_4]^2 + k_2[\text{H}_2\text{SO}_4]) \quad (5)$$

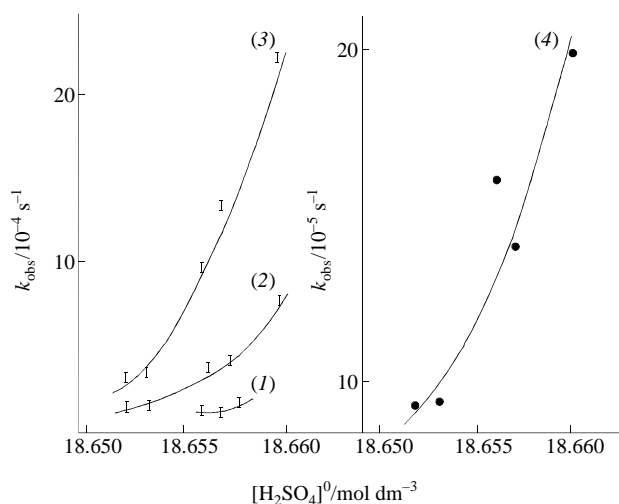
This fact has been found experimentally for the first time for the dissociation reactions of metalloporphyrins and their azabenzene analogues – the metallophthalocyanines. Each of the mentioned routes of the reaction can be interpreted within the bounds of mechanisms already known for other metalloporphyrins: S<sub>EN</sub>3<sup>9</sup> (route 1 with  $k_1$  constant) and S<sub>N</sub>2<sup>15</sup> (route 2 with  $k_2$  constant). The corresponding transition states are: [(Cl)<sub>2</sub>MTPP·2H<sub>2</sub>SO<sub>4</sub>]<sup>‡</sup> and [(Cl)<sub>2</sub>MTPP·H<sub>2</sub>SO<sub>4</sub>]<sup>‡</sup>. It must be pointed out that the dissociation reaction for the tin complex proceeds along route 1 under the action of H<sub>2</sub>SO<sub>4</sub> molecules but not H<sub>3</sub>O<sup>+</sup> as for metallophthalocyanines.

In case of (Cl)<sub>2</sub>GeTPP  $k_{\text{obs}}$  constants (Figure 3) are in linear correlation with [H<sub>2</sub>SO<sub>4</sub>]<sup>2</sup> ( $r = 0.97$ ):

$$-dC_{(\text{Cl})_2\text{GeTPP}}/d\tau = k_1[(\text{Cl})_2\text{GeTPP}][\text{H}_2\text{SO}_4]^2 \quad (6)$$

where  $k_1 = (1.4 \pm 0.2) \times 10^{-3}$  and  $(5.5 \pm 1) \times 10^{-3} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  at 323 and 333 K, respectively,  $E_a = 121 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -69 \text{ J mol}^{-1} \text{ K}^{-1}$ . Comparison of equations (5) and (6) shows that the reaction route with  $k_2$  constant is imperceptible for the dissociation of the germanium complex.

The stability of the metalloporphyrins discussed in the mixed solvent H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O in the Brand region (where H<sub>3</sub>O<sup>+</sup> concentration is high) as well as specific rate equation (5), are apparently caused by the strong covalent bonding of acido ligands (Cl) in the coordination sphere. Dissociation of M–Cl bonds of complexes (Cl)<sub>2</sub>MTPP probably takes place only in media of maximum dielectric permeability, i.e. 99.94–100% H<sub>2</sub>SO<sub>4</sub>.



**Figure 3** Dependence of the observed rate constant for dissociation of (Cl)<sub>2</sub>GeTPP vs. H<sub>2</sub>SO<sub>4</sub> concentration. T/K: (1) 313, (2) 323, (3) 333, (4) 298.

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