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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.[1] Metalloporphyrins with composition MP (P = porphyrin dianion, M = doubly-charged metal cation) are less stable[2–4] and undergo destruction, being dissolved in concentrated H_2SO_4. Before any detailed investigations into the stability of acidoporphyrin complexes of highly charged metal cations of composition $(X)_{n-2}MP$ (X = single-charged acido ligand) appeared it had been assumed[5] that all metalloporphyrins were unstable in sulfuric acid. It was shown[6–8] that complexes of tetraphenylporphin $(X)_{n-2}MTPP$ 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_2SO_4. However, it was difficult to identify the complexes in the sulfuric acid solution because they form an H-associate $(X)_{n-2}MTPP\cdots H^+_{Solv}$ 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_2SO_4 or its absence has been found.[9] 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)germaniumtetraphenylporphin $(Cl)_2GeTPP$ and (dichlorine)tintetraphenylporphin $(Cl)_2SnTPP$.

$(Cl)_2GeTPP$ was obtained as described in ref. 10 by reaction of the complex formation of H_2TPP with $GeCl_4$ in quinoline at 510 K under a nitrogen atmosphere. $(Cl)_2SnTPP$ was obtained as described in ref. 11 by an analogous reaction of H_2TPP with $SnCl_2$ in boiling dimethylformamide. The tin complex was purified by chromatography on an Al_2O_3 column using $CHCl_3$ and the germanium complex using $CHCl_3$ and then diethyl ether. UV/VIS spectra of the complexes coincide with literature data[12,13] λ_{max}/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 $CHCl_3$, respectively. The complexes are partially dissolved in concentrated H_2SO_4, 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_{max}/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.

$(Cl)_2MTPP$ undergoes dissociation [reaction (1)] at a spectrophotometrically measured rate only in media with a maximum proton donor particles content: in H_2SO_4 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.

$$(Cl)_2MTPP + 4H^+_{Solv} \longrightarrow H_4TPP^{2+} + (Cl)_2M^{2+}_{Solv} \qquad (1)$$

Solvent H_2SO_4–H_2O with acid content 99.94–99.98% was prepared by the weight method from 100% H_2SO_4 and H_2SO_4 with definite concentration. Experimental constants of the dissociation rate k_{obs} were defined from dependences ln C_0/C_τ–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 $(Cl)_2SnTPP$ in 100% H_2SO_4 and $(Cl)_2GeTPP$ in 99.93–100%

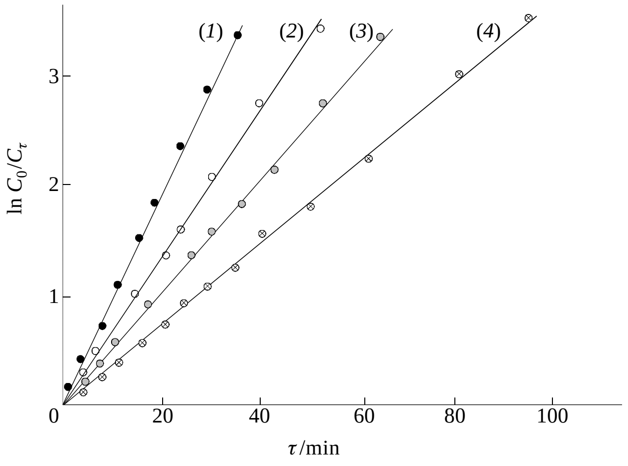

Figure 1 Dependence of the logarithm of the ratio of initial and current concentrations of metalloporphyrin ln C_0/C_τ *vs.* time τ. $C_{H_2SO_4}$ (%): (*1*), (*3*) 99.96; (*2*), (*4*) 99.94. *T*/K: (*1*), (*2*) 362; (*3*), (*4*) 358.

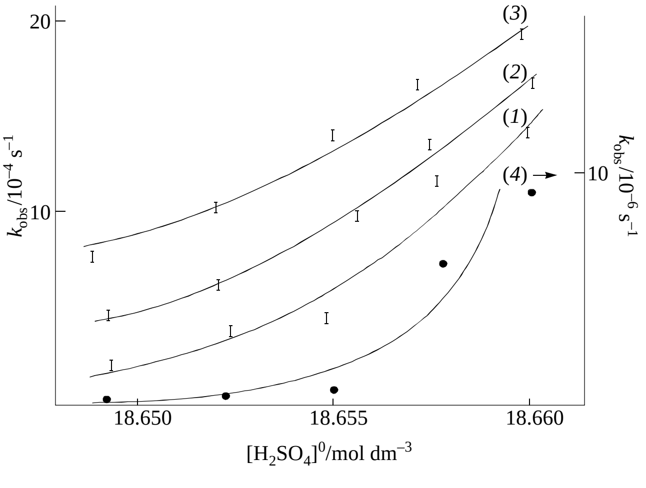

Figure 2 Dependence of the observed rate constant for dissociation of $(Cl)_2SnTPP$ *vs.* H_2SO_4 concentration. *T*/K: (*1*) 353, (*2*) 358, (*3*) 362, (*4*) 298.

H_2SO_4 were published earlier,[5,14] and values of k_{obs} for dissociation of the tin complex in H_2SO_4–H_2O 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):

$$-dC_{(Cl)_2MTPP}/d\tau = k_{obs}[(Cl)_2MTPP] \qquad (2)$$

However, the influence of the H_2SO_4 concentration complicates the rate equation. As shown in Figure 2, the plot of the observed rate constant for the dissociation of $(Cl)_2SnTPP$ *vs.* $[H_2SO_4]$ 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):

$$k_{obs} = k_1[H_2SO_4]^2 + k_2[H_2SO_4] \qquad (3)$$

$$k_{obs}/[H_2SO_4] = k_1[H_2SO_4] + k_2 \qquad (4)$$

The values of k_1 and k_2 obtained from the linear dependence of $k_{obs}/[H_2SO_4]$ *vs.* $[H_2SO_4]$ [correlation coefficient $r = 0.97$; selection of pairs of values of argument and function $(2–3)\times 5$] within the least-squares method are $(5\pm1)\times10^{-3}$ dm^6 mol^{-2} s^{-1} and $(1.0\pm0.2)\times10^{-2}$ dm^3 mol^{-1} 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_{obs} and $[H_3O^+]$, $[H_3O^+]^2$, $[H_2SO_4]$ or $[H_2SO_4]^2$ leads to worse correlation coefficients. The general rate equation (5) testifies that the dissociation reaction of the tin complex proceeds along two parallel routes.

$$-dC_{(Cl)_2SnTPP}/d\tau = [(Cl)_2SnTPP](k_1[H_2SO_4]^2 + k_2[H_2SO_4]) \qquad (5)$$

This fact has been found experimentally for the first time for the dissociation reactions of metalloporphyrins and their azabenzo analogues – the metallophthalocyanines. Each of the mentioned routes of the reaction can be interpreted within the bounds of mechanisms already known for other metalloporphyrins: $S_{EN}3$[9] (route 1 with k_1 constant) and S_N2[15] (route 2 with k_2 constant). The corresponding transition states are: $[(Cl)_2MTPP\cdot 2H_2SO_4]^{\neq}$ and $[(Cl)_2MTPP\cdot H_2SO_4]^{\neq}$. It must be pointed out that the dissociation reaction for the tin complex proceeds along route 1 under the action of H_2SO_4 molecules but not H_3O^+ as for metallophthalocyanines.

In case of $(Cl)_2GeTPP$ k_{obs} constants (Figure 3) are in linear correlation with $[H_2SO_4]^2$ ($r = 0.97$):

$$-dC_{(Cl)_2GeTPP}/d\tau = k_1[(Cl)_2GeTPP][H_2SO_4]^2 \qquad (6)$$

where $k_1 = (1.4\pm0.2)\times10^{-3}$ and $(5.5\pm1)\times10^{-3}$ dm^6 mol^{-2} s^{-1} at 323 and 333 K, respectively, $E_a = 121$ kJ mol^{-1}, $\Delta S^{\neq} = 69$ J mol^{-1} 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_2SO_4–H_2O in the Brand region (where H_3O^+ 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 $(Cl)_2MTPP$ probably takes place only in media of maximum dielectric permeability, *i.e.* 99.94–100% H_2SO_4.

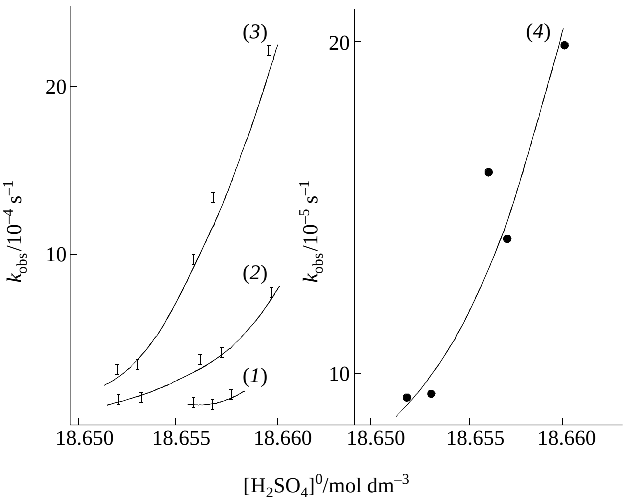

Figure 3 Dependence of the observed rate constant for dissociation of $(Cl)_2GeTPP$ *vs.* H_2SO_4 concentration. *T*/K: (*1*) 313, (*2*) 323, (*3*) 333, (*4*) 298.

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