Inorganica Chimica Acta, *138* (1987) 139–143

A Study of Complex Formation between Differently Charged Free-base Porphyrins and Samarium Porphyrins

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(Received April 6, 1987)

Abstract

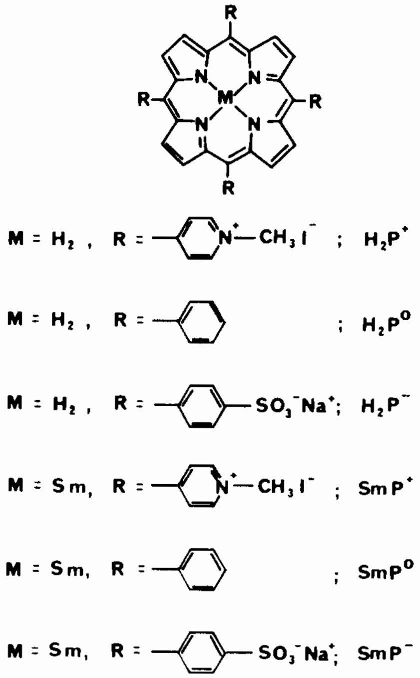
The intramolecular interaction and complex formation among anionic, neutral and cationic free-base mesotetraphenylporphyrins and their samarium(III) complexes have been investigated in dimethyl sulfoxide solutions. The equilibrium constants (range from 0.1×10^6 to 5×10^6 M^{-1}) indicate appreciable interactions, however neutral samarium porphyrin does not interact with free-base porphyrins. Samarium anionic porphyrin also does not interact with neutral and anionic free-base porphyrins. These results are discussed in terms of competition among coulombic forces, polarisation effects and $\pi-\pi$ interactions between two macrocycles.

Introduction

The study of the metalloporphyrins has been an active field of research for several decades because of their involvement in various chemical and biological processes. It is also known that lanthanide complexes have found prominent use as paramagnetic and fluorescence probes of molecules with biological interest [1]. The lanthanide porphyrin complexes seem to be very useful for these purposes [2], however their chemistry is practically unknown.

It was concluded that many free-base porphyrins and metalloporphyrins may be present in water solutions as dimers or higher, more complicated aggregates [3–5], although these phenomena are rarely observed for the nonaqueous solutions [6, 7]. It was established in our laboratory that there is possible formation of 'face-to-face' complexes between positively charged metalloporphyrins [Mn^{III}, Zn^{II}, Cu^{II} tetrakis(4-*N*-methylpyridyl)porphyrin] and negatively charged metallophthalocyanines (Mn^{II} and Cu^{II} 4,4′,4″,4‴-tetrasulfonated phthalocyanine) or metalloporphyrin [Mn^{III}tetrakis(sulfonatophenyl)porphyrin] [8, 9]. The formation of these adducts, which have a stoichiometry of one-to-one, involve intensive coulombic interactions between two differently charged macrocycles. Other short reports have appeared recently dealing with the interaction of cationic and anionic porphyrins in mixed water–organic solvents [10, 11]. However, to our knowledge, there is no information on the mutual interactions of free base porphyrins and metallated porphyrins, with the metal in oxidation state III and out of plane with respect to the macrocycle.

This paper deals with the results of the study in an aprotic medium on the mutual interaction and complex formation between differently charged free-base porphyrins [*meso*-tetraphenylporphyrin, *meso*-tetra(4-*N*-methylpyridyl)porphyrin or tetrasodium-*meso*-tetra(4-sulfonatophenyl)porphyrin] and samarium complexes of these porphyrins (compounds **1–6**)



Samarium porphyrins were studied, because it was known that all the lanthanides are inserted 'out-of-plane' with respect to the porphyrin ring [12–14] and it was interesting to investigate how these kinds of compounds would behave during double complex formation processes.

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0020-1693/87/$3.50

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Experimental

Materials

Tetraphenylporphyrin **2** was prepared according to a procedure developed by Adler and coworkers [15–17]. Its purity was checked by TLC and UV–Vis spectroscopy. *Meso*-tetra(4-*N*-methylpyridyl)porphyrin **1**, tetrasodium-*meso*-tetra(4-sulfonatophenyl)-porphyrin dodecahydrate **3**, and samarium acetylacetonate were used as supplied by Strem Chemicals, Inc.

Synthesis of Sm^{III} Porphyrins

The tetramethylpyridyl porphyrin complex of samarium **4** has not been described previously. For the synthesis of this compound we used a modification of the procedure developed for the cerium octaethylporphyrin by Buchler [14]. A mixture of hydrated $Sm(acac)_3$ (100 mg) and free-base porphyrin **1** (50 mg) in 1,2,4-trichlorobenzene was heated in reflux under argon for 4 h. The course of the reaction was followed periodically by UV–Vis spectra. After completion of the reaction 1,2,4-trichlorobenzene was quickly evaporated off under reduced pressure. This operation should be done with care as porphyrin complexes of lighter lanthanides are very susceptible to demetalation when overheated. After being vacuum dried overnight, the reaction mixture was dissolved in CH_2Cl_2 and applied to the top of a neutral grade Al_2O_3 (Merck) column saturated with CH_2Cl_2. The unreacted free-base porphyrin was eluted with pyridine, and samarium tetramethylpyridylporphyrine was eluted with dimethyl sulfoxide (DMSO). Unreacted $Sm(acac)_3$ remains adsorbed on the column. The DMSO solution of **4** was evaporated under reduced pressure, and the crystals, vacuum dried over P_2O_5. *Anal.* Calc. for SmTMePyP·$10H_2O$ ($SmC_{49}H_{63}N_8J_4O_{12}$): C, 36.43; H, 3.99. Found: C, 36.54; H, 3.71%. UV–Vis: [λ_{max}, $\epsilon((M^{-1}\ cm^{-1}) \times 10^{-3})$]: 430 (34.1), 514 (2.4), 560 (2.75), 590 (1.4).

The tetraphenylporphyrin complex of samarium **5** was synthesized by the method described by Horrocks and Wong [13, 18]. *Anal.* Calc. for SmTPP-(acac), ($SmC_{49}H_{35}N_4O_2$): C, 68.27; H, 4.06. Found: C, 67.28; H, 4.08%. UV–Vis: [λ_{max}, $\epsilon((M^{-1}\ cm^{-1}) \times 10^{-3})$]: 430.6 (35.4), 520 (4.8), 564 (13.4), 599 (5.7).

The samarium complex of tetrasulfonatophenylporphyrin **6** was prepared by the procedure described previously by Horrocks and Hove [12] for the same complexes but with heavy lanthanides. When the synthesis is carried out in imidazole melt under argon, care should be exercised in order to avoid the hydrolysis of the samarium. *Anal.* Calc. for Na_4-SmTPPS(acac)·$12H_2O$ ($Na_4SmC_{49}H_{55}N_4O_{26}S_4$): C, 39.59; H, 3.77. Found: C, 37.80; H, 3.65. UV–Vis: [λ_{max}, $\epsilon((M^{-1}\ cm^{-1}) \times 10^{-3})$]: 432 (16.5), 520 (2.2), 562 (7.4), 602 (3.3).

Solutions

All the solutions of free-base porphyrins and samarium porphyrins were prepared in dimethyl sulfoxide (obtained from Merck) which was additionally dried by 3 Å molecular sieves and degassed with argon. The solutions were kept under argon in the dark to prevent their possible photochemical decomposition. The solutions were originally prepared in concentrations of 10^{-4} M and were diluted to 10^{-5} or 10^{-6} M just before performing the experiments.

Spectra

Visible and ultraviolet spectra were recorded with a Perkin-Elmer Lambda-5 spectrophotometer using 1 cm quartz cells. The studies reported here were done at 22 ± 1 °C.

Methods

Control of complex formation and determination of their stoichiometry were carried out according to Job's method of continuous variation [19, 20]. This method is based on spectrophotometric analysis of mixture of equimolar solutions in the ratio of x volumes of the first solution to $1 - x$ of the second solution (in which the ratio of two porphyrins [P]: [P′] varies in increments from 10:0 up to 0:10) were obtained.

The stability constants of the one-to-one complexes were measured found from Beer's law experiments. The change in absorbance was measured for the series of solutions in which concentration of the compound P was constant and the concentration of compound P′ increased in increments. Results were compared with those obtained from analogous experiments in which the compound P was exchanged for DMSO, and the compound P′ was added to DMSO in the same portions as in the previous experiments. In a complementary experiment the mixing of the solutions was conducted in the opposite way. The concentration of compound P′ was fixed and firstly P was added to P′, later P was added to DMSO in the same ratio. Eventually, for every pair of compounds two graphs were obtained: in the first, absorbance was plotted against concentration of compound P′ (two curves P + P′ and DMSO + P′), in the second absorbance was plotted against concentration of P(P′ + P and DMSO + P).

Results and Discussion

All the spectral measurements were carried out in dimethyl sulfoxide solutions. DMSO was chosen as a solvent because according to the literature, in DMSO solutions deviations from Beer's law generally have not been observed, neither for porphyrins nor for metalloporphyrins [4], which means that agglomeration does not occur in this solvent. The dielectric constant of DMSO ($D = 46.7$) is sufficient to induce intermolecular interaction. Additionally it is known that free-base tetrasulfonatophenylporphyrin dimerises in water at higher concentration [3]. Recently, it was reported that tetramethylpyridylporphyrin also dimerises in aqueous solutions [21, 22]. In this instance Beer's law experiments were carried out on all compounds used and it was concluded that tetrasulfonatophenylporphyrin also dimerises in DMSO solutions at more or less the same concentration of porphyrin as in water. The apparent dimerisation constant was calculated and its value (1.8×10^4 M^{-1}) is lower comparable however to that obtained by Pasternack *et al.* in aqueous solution [3]. Deviation from a Beer's law straight line was found as well in the case of tetrasulfonatophenyl samarium porphyrin and the dimerisation constant was calculated (0.5×10^6 M^{-1}). In the case of other porphyrins and samarium porphyrins (including tetramethylpyridylporphyrin) in DMSO solution deviations from Beer's law were not observed. For the complex formation studies, we have chosen to work in the concentration region where self-association does not occur. Because the compounds (even tetrasulfonatophenyl free-base porphyrin and tetrasulfonatophenyl samarium porphyrin at the concentrations being considered) conform to Beer's law at the low concentration of solutions used in our experiments (10^{-6}–10^{-5} M) the concentration has been assumed equal to the activity (ionic strength = 0) obtained by following modified Job's method are presented. Stoichiometry of the complexes formed from two different porphyrins were obtained by a modification of Job's method as shown for example in Fig. 1 for the porphyrins **1** and **4**.

In every case, where we have observed an interaction (Table I) the new complexes have a stoichiometry 1:1. For the pairs **1**–**5**, **2**–**5**, **3**–**5**, **2**–**6**, **3**–**6** and **5**–**6** straight lines were obtained for the Job's plots indicating no interactions between these porphyrins.

The self-association constant (Table I) for the dimerising porphyrins **3** and **6** were determined by the method described in one of our previous papers [23]. The calculations were carried out according to the Beer's law experiments.

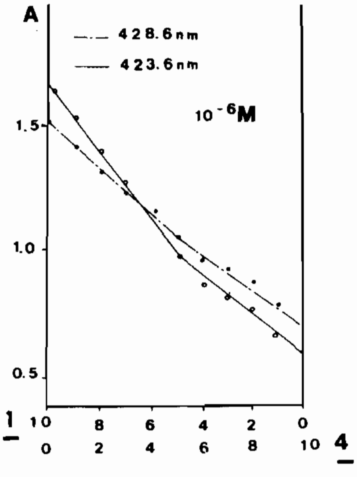

Fig. 1. Example of determination of stoichiometry of the complex (case of porphyrins **1** and **4**).

The association constants of the double complex formed from the two porphyrins P and P′ were calculated according to the formation equilibrium:

$$P + P' \underset{}{\overset{K}{\rightleftarrows}} PP' \tag{1}$$

using the following relationship:

$$\Delta A = \Delta\epsilon \frac{K([P]_0 + [P']_0) + 1 - \sqrt{K^2([P]_0 - [P']_0)^2 + 2K([P]_0 + [P']_0) + 1}}{2K} \tag{2}$$

where:

$[P]_0$ and $[P']_0$) are the analytical concentrations of the porphyrins P and P′;

$$\Delta\epsilon = \epsilon_P + \epsilon_{P'} - \epsilon_{PP'} \tag{3}$$

ϵ_P, $\epsilon_{P'}$ and $\epsilon_{PP'}$ are the extinction coefficient, ΔA represents the deviation of the absorbance from linearity (Fig. 2). In the systems where the complex formation does not take place, the deviation of absorbance from the linearity was not observed, and the concentration dependence curve of mixture P + P′

TABLE I. Association constants[a] for Analysed Pairs of Compounds[b]

Compounds	H_2P^+ (1)	H_2P^0 (2)	H_2P^- (3)	SmP^+ (4)	SmP^0 (5)	SmP^- (6)
H_2P^+ (**1**)	n.s.					
H_2P^0 (**2**)	0.9	n.s.				
H_2P^- (**3**)	1.4[c]	0.4	0.018[d]			
SmP^+ (**4**)	5.0	0.47	0.51	n.s		
SmP^0 (**5**)	n.i.	n.i.	n.i.	0.1	n.s.	
SmP^- (**6**)	1.5	n.i.	n.i.	1.0	n.i.	0.5

[a] In 10^{-6} M^{-1} (±10%). [b] n.s. = no self-association, n.i. = no interaction. [c] Value found by Ojadi *et al.* for 1:1 water–acetone solution is 1.1×10^8 M^{-1} [10]. [d] Value found by Pasternack *et al.* for water solution is 5×10^4 M^{-1} [3].

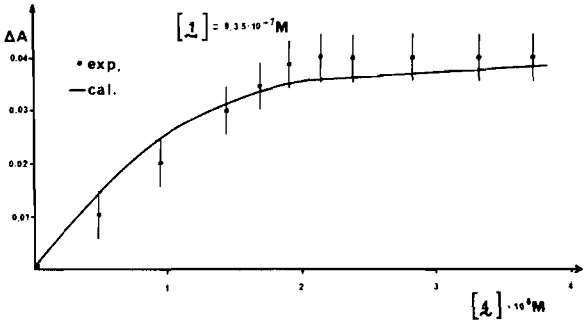

Fig. 2. A plot of the calculated curve ΔA *vs.* SmP^+ (4) concentration compared to experimental points (for notations see text).

is parallel to the Beer's law curve (DMSO + P′) within an uncertainty of about 0.0025 absorbance unit. The calculated plot of ΔA against the concentration of P′ (concentration of P was constant) is in good agreement with our experimental points (Fig. 2). All the calculated stability constants are presented in Table I. We may generally remark that either the self-association of the association constants have a lower value in DMSO than in water solutions. For example, for the free-base tetrasulfonatophenylporphyrin **3** we have found a self-association constant of 1.8×10^4 M^{-1} in DMSO, while the constant for this porphyrin in H_2O has a value of 5×10^4 M^{-1} [3]. For the system free-base tetramethylpyridylporphyrin **1** and free-base tetrasulfonatophenylporphyrin **3** a value 1.4×10^{-6} M^{-1} was found compared to 1.1×10^8 M^{-1} found by Ojadi *et al.* [10] for 1:1 water– acetone solution. This arises from the fact the solvating ability of DMSO is higher than that of water.

In our studies all the cases where the pairs of compounds with an oppositely charged peripheral group were considered, strong interaction between macrocycles was found (H_2P^+–H_2P^-, SmP^+–SmP^-, H_2P^+–SmP^- and H_2P^-–SmP^+). Analysis of the stability constants for plus-minus charged porphyrin systems suggests that the presence of Sm^{III} in porphyrin ring only slightly influences these coulombic interactions.

The coulombic interactions disappear when we consider SmP^- with a neutral macrocycle such as H_2P^0 or SmP^0. In the case of SmP^+ we are able to observe different interactions. In fact analysis of the equilibrium constants for the pairs SmP^+ –SmP^0, SmP^+ –H_2P^+ and SmP^+ –H_2P^0 shows significant interactions, particularly strong for SmP^+ –H_2P^+.

Neither association nor self-association between non charged porphyrins was observed. This phenomenon is known and was explained previously [4] by steric hindrances due to the perpendicular orientation of the phenyl group in the tetraphenylporphyrin. Neutral macrocycles derived from tetraphenylporphyrin do not interact at all except in the case of high spin ferric tetraphenylporphyrin [6].

In the case of the two negatively charged porphyrins strong self association for H_2P^- (the constant is comparable to the one for water solution [3] and also for SmP^- was observed. For the other porphyrins interactions or non interactions of macrocycles are due to the combinaison of three factors: (i) back polarisation; (ii) π–π interaction; (iii) steric hindrances.

The two first factors strongly favour the formation of adduct species between two porphyrins but they are in competition with the intermolecular steric strain due to the hindrance of phenyl groups size of the metal and axial ligation.

In conclusion our results indicate that complexes between differently charged porphyrins are formed even when large-sized metal ions such as samarium-(III) are complexed into the porphyrin ring and even when non charged porphyrins are implicated. In these systems, however, back polarisation and metalloporphyrin geometry should be considered besides the coulombic forces which play the most important role.

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Appendix

Derivation of Relationship (2)

The notations are as given in the text. The equilibrium constant can be expressed:

$$K = \frac{|PP'|}{|P|\,|P'|} \tag{4}$$

The overall absorbance is

$$A = \epsilon_P|P| + \epsilon_{P'}|P'|\epsilon_{PP'}|PP'| \tag{5}$$

$$\text{As } |P_0| = |P| + |PP'| \tag{6}$$

and

$$P'_0 = |P'| + |PP'| \tag{7}$$

we can write

$$A = \epsilon_P(|P_0| - |PP'|) + \epsilon_{P'}(|P'_0| - |PP'|) + \epsilon_{PP'}|PP'| \tag{8}$$

or

$$A = \epsilon_P|P_0| + \epsilon_{P'}|P'_0| - (\epsilon_P + \epsilon_{P'} - \epsilon_{PP'})|PP'| \tag{9}$$

As $\Delta A = (A - \epsilon_P|P_0| + \epsilon_{P'}|P'_0|)$ represents the deviation of the absorbance from linearity (9) can be written

$$\Delta A = (\epsilon_P + \epsilon' - \epsilon_{PP'})|PP'| \tag{10}$$

Substituting relationships (6) and (7) in (4), eqn. (11) is easily obtained:

$$[PP'] = K(|P_0|\,|P'_0| - |PP'|(|P_0| + |P'_0|) + |PP'|^2) \tag{11}$$

or

$$K|PP'|^2 - |PP'|\,[K(|P_0| + |P'_0|) + 1] + K|P_0|\,|P'_0| = 0 \tag{12}$$

Solving this equation gives eqn. (13)

$$|PP'| = \frac{K(|P_0| + |P'_0|) + 1 - \sqrt{K^2(|P_0| - |P'_0|)^2 + 2K(|P_0| + |P'_0|) + 1}}{2K} \tag{13}$$

Including eqn. (13) in eqn. (10) we obtain relationship (2).