

Metalloporphyrins Obtained in Aqueous Solution Based on the 5,10,15, 20-Tetra-*p*-(*N,N*-dimethyl)anilinoporphyrin

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Abstract

The modified method of preparation of water soluble metalloporphyrins is presented. As a ligand 5,10,15,20-tetra-*p*-(*N*-ethyl-*N,N*-dimethyl)anilinoporphyrinium disulphate was used. The structure of the obtained metalloporphyrins for the following metal cations: Mg(II), Zn(II), Cd(II), Ag(II), Ru(II), Rh(II), Ni(II), Fe(III), Mn(III), Co(III) and Sn(IV), was confirmed by electron, IR spectra and elemental analyses.

Introduction

Some recent studies on the conversion and storage of solar energy have proposed water-soluble zinc(II) and tin(IV) porphyrinates as useful agents in photo-reduction [1–4], and the manganese(III) porphyrinates in photooxidation of water [5]. On the other hand, electrochemical studies on water soluble metalloporphyrins have shown their utility as electrode modifiers. The glassy carbon electrodes were chemically modified using iron(III), manganese(III) and cobalt(III) porphyrinates [6–8] and appeared to be useful in the electrocatalytical reduction of oxygen.

The methods of preparation of metalloporphyrins in acidic, basic and neutral nonaqueous media and in aqueous solution have been presented in literature [9–12]. Most often in synthesis of porphyrin complexes one of the following compounds was applied:

5,10,15,20-tetra-*p*-(*N,N*-dimethyl)anilinoporphyrin (TAPH₂), Fig. 1a;

5,10,15,20-tetra-*p*-pyridylporphyrin (TPyPH₂), Fig. 1b;

5,10,15,20-tetra-*p*-sulphonatophenylporphyrin (TSPPH₂), Fig. 1c;

5,10,15,20-tetra-*p*-carboxyphenylporphyrin (TCPPH₂), Fig. 1d.

In order to transform TPyPH₂ and TAPH₂ and their respective complexes into water soluble compounds, they were usually treated with methyl

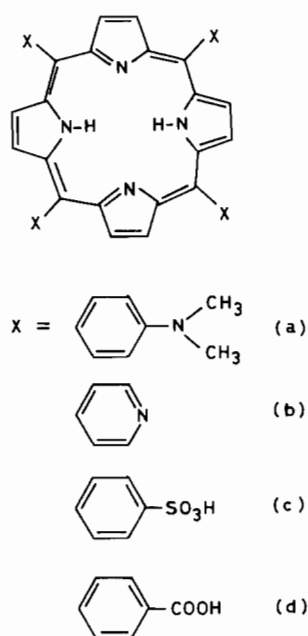


Fig. 1. (a) TAPH₂, (b) TPyPH₂, (c) TSPPH₂, (d) TCPPH₂.

iodide [11–16]. It is known that some of the quaternary salts obtained in this way are water-soluble only within a limited pH range, especially the TAPH₂ derivatives [8].

In this paper, a modified method of preparation of metalloporphyrins in aqueous medium is presented. The method employs for the first time 5,10,15,20-tetra-*p*-(*N*-ethyl-*N,N*-dimethyl)anilinoporphyrinium disulphate (TEAPH₂) as a ligand. With this compound, it is possible to obtain the water-soluble porphyrin complexes of all transition metals in the full range of pH values.

Experimental

Preparation of TEAPH₂

10 cm³ of (EtO)₂SO₂ (Fluka) was added to 3 g (0.004 mol) of TAPH₂, obtained by the Datta–Gupta

TABLE I. Absorption Bands, λ_{\max} , and Absorption Coefficients, ϵ , of the Electron Spectra for the Metalloporphyrins Obtained (water solution, pH 4, room temperature) and the Results of Elemental Analysis

Compound	λ_{\max} ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$)	Elemental analyses, found (calc.)		
		%C	%H	%N
TEAPH ₂	414(38.45) 518(1.59) 552(0.53) 583(0.60) 637(0.37)	65.0 (65.8)	6.7 (6.4)	10.5 (10.2)
TEAPMg	422(31.87) 518(0.45) 559(1.99) 599(0.59)	64.0 (64.4)	6.3 (6.1)	10.3 (10.0)
TEAPZn	422(36.38) 520(0.40) 559(2.03) 599(0.64)	59.8 (62.1)	6.1 (5.9)	10.1 (9.7)
TEAPCd ^a	436(33.15) 541(0.42) 578(1.26) 621(1.04)	58.1 (59.7)	6.0 (5.6)	9.4 (9.3)
TEAPAg	420(28.92) 542(1.05)	60.1 (60.0)	5.8 (5.7)	9.5 (9.3)
TEAPRu(Py) ₂	421(19.95) 498(0.27) 532(1.58) 567(0.31)	63.8 (63.7)	6.1 (5.9)	10.8 (10.6)
TEAPRh	419(15.45) 531(1.34) 570(0.28)	60.1 (60.3)	5.9 (5.7)	9.5 (9.4)
TEAPNi	410(22.96) 529(1.35)	62.4 (62.6)	6.0 (5.8)	9.9 (9.7)
TEAPFe(OH)	394(9.98) 529(0.96) 667(0.25)	61.5 (62.7)	6.1 (6.0)	9.9 (9.7)
TEAPMn(OH)	376(4.78) 399(4.67) 466(8.97) 565(0.98) 596(0.53)	62.1 (62.7)	6.2 (6.0)	9.8 (9.7)
TEAPCo(OH)	427(8.53) 541(1.22)	62.0 (62.4)	6.2 (6.0)	9.8 (9.7)
TEAPSn(OH) ₂	420(30.69) 518(0.31) 556(1.63) 595(0.54)	59.1 (59.4)	5.8 (5.8)	9.5 (9.2)

^aIn basic aqueous solution of KOH at pH 11.

method [17], and then the mixture was heated to the boiling point under continuous stirring. After the crude product was cooled, it was filtered, washed with acetone and crystallized from EtOH. Yield 98%.

Preparation of TEAPM (M = Mg(II), Zn(II), Cd(II), Ni(II), Ag(II), Ru(II), Rh(II), Mn(III), Fe(III), Co(III), and Sn(IV))

10 cm³ of 0.05 M aqueous solution of TEAPH₂ was added to 10 cm³ of 0.25 M aqueous solution of the respective salt. In the cases of Mg(II), Zn(II), Cd(II), Ni(II), Mn(III) and Co(III), acetic salts (POCh) were used. In the cases of Fe(III), Ag(II), Ru(II), Rh(II) and Sn(IV), the Mohr Salt (Fluka), AgNO₃ (POCh), RuCl₃ (Johnson Matthey Chemicals), RhCl₃ (Fluka), and SnCl₂ (POCh) were employed. The obtained solution was heated up to 80 °C and kept in a dark place at this temperature for about 0.5 h. During this time, the pH of the mixture was adjusted to 5. The end of the reaction is indicated by a change in colour from green to red. After this, the mixture was dried under vacuum. In the case of the metalloporphyrin of Ru(II), 10 cm³ of pyridine (POCh) was added, heated to 80 °C, and dried under vacuum again. The residue was dis-

solved in MeOH. The solution was filtered and then the product was precipitated by acetone. The crystals were separated and crystallized twice from MOH. Yield 40–50%. The resulting electronic spectra and elemental analyses for the obtained metalloporphyrins are presented in Table I.

The spectroscopic studies in the visible range were performed by means of SPECORD UV–Vis (Carl Zeiss, Jena) spectrometer. The elemental analysis was carried out using type 240 Perkin-Elmer analyzer. The IR spectra were obtained by means of the ATR technique using a SPECORD 71 IR (Carl Zeiss, Jena) spectrophotometer with reflection element made from KRS-5.

Results and Discussion

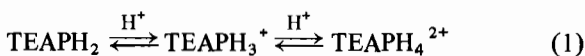
TAPZn, TAPMn(CH₃COO), TAPCo(CH₃COO) were prepared according to Adler's method in acidic solution [9]. This method did not allow the formation of TAPMg, due to its low stability in acidic solutions [9]. The product obtained during the heating of porphyrin with the acetate of the respective metal in CH₃COOH usually contains some unreacted porphyrin. It is possible that associates

of TAPH₂ with CH₃COOH, which can be formed in course of the process, stop the coordination reaction of the respective metal cation.

In order to obtain water-soluble metalloporphyrins from TAPZn, TAPMn(CH₃COO), and TAPCo(CH₃COO), *N*-alkylation was employed. Ethyl bromide (EtBr), methyl iodide (MeI) and diethyl sulphate ((EtO)₂SO₂) have been used as *N*-alkylating agents. It was found that heating the metalloporphyrins with (EtO)₂SO₂ leads to their demetalation. In the case of using EtBr and MeI, practically all the bromide quaternary salts of these metalloporphyrins are insoluble in water. Only TMAPMn(CH₃COO)I₄ dissolves in water in the whole range of pH values, while TMAPCo(CH₃COO)I₄ dissolves only in acidic solutions. Another approach can be made during the first step of the synthesis when a water soluble ligand is prepared [10–12]. Then the coordination of the respective metal cation can be performed simply in water.

In order to prepare the water-soluble ligand, TAPH₂ was *N*-alkylated with MeI, (EtO)₂SO₂ and dimethyl sulphate ((MeO)₂SO₂). In the case of using MeI, the rate of *N*-alkylation is very low [14]. If the (MeO)₂SO₂ was applied, the reaction product exhibited absorption spectra that were different from the water soluble porphyrins. The probable reason for this is that there is alkylation not only of the amine-groups, but also of the nitrogen atoms within the porphyrin ring. The best results were obtained when (EtO)₂SO₂ was employed. TEAPH₂ obtained in this way exhibits solubility in water in the whole range of pH values.

The absorption spectra of aqueous solutions of TEAPH₂ change with pH, similar to those of TMAPH₂ [7]; this can be explained by the following reactions:



According to this, the form of double-protonated porphyrin exists in aqueous solution at pH ≤ 2.

We have found complexogenic properties of aqueous solutions of TEAPH₂ at pH > 2. Figure 2a shows absorption spectra of TEAPH₂ in H₂O, and its spectra when (CH₃COO)₂Co was added (Fig. 2b), whereas Fig. 2c shows spectra of the compound obtained after its reduction with ascorbic acid. The band at λ = 427 nm indicates the presence of cobalt(III) porphyrinate, whereas the presence of cobalt(II) porphyrinate at λ = 416 nm is confirmed [8].

The method presented above modifies the procedure described earlier [2, 12, 14], which employs (EtO)₂SO₂ instead of MeI. The advantage of using (EtO)₂SO₂ is the possibility of preparing metalloporphyrins for a wider group of metals. This is due to the fact that, in general, sulphates of all transi-

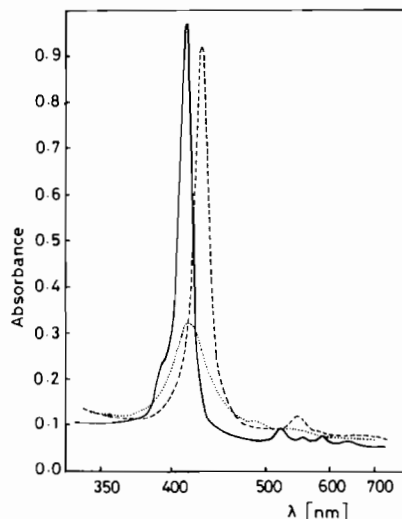


Fig. 2. Absorption spectra: (a) 2.5×10^{-6} M TEAPH₂ in H₂O at room temperature, at pH 4 (—); (b) after addition of excess (CH₃COO)₂Co and heating to 80 °C (---); (c) after reduction with ascorbic acid (·····).

tion metals exhibit very good water solubility, in contrast to their halides. Further, all metalloporphyrins we have prepared are water-soluble in the whole range of pH, in contrast to, for example, TMAPCo(OH)Cl₄ which is soluble only at pH ≤ 2 [8]. Moreover, the use of (EtO)₂SO₂ makes the preparation of metalloporphyrins much faster, mainly due to the fact that the anion exchange step is not necessary and the quaternisation process is very fast.

In the process of metal coordination, the highest yield was obtained in acetic salts solutions (Zn, Mg, Mn, Cd, Co, Ni). When using chlorides, nitrates or sulphates, the addition of a base was necessary to correct the pH of reaction mixture to pH 5 (Ru, Rh, Sn, Cd, Ag, Fe).

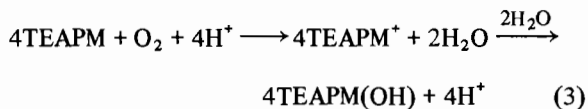
In order to confirm the degree of oxidation of the obtained metalloporphyrins, spectrophotometry in visible region was applied. The results were in good agreement with those obtained for known metalloporphyrins of the respective metals [2, 3, 6–8, 10–12, 18–28].

During the preparation process, some side reactions can occur. The sequence of possible reactions after the coordination process is presented by following schemes:

Coordination of the metal cation



Oxidation of metalloporphyrin



Reduction of metalloporphyrin



Dimerization of metalloporphyrin



The oxidation process takes place when $M = \text{Fe}$, Mn , Co , Ag , and Sn ; reduction occurs when $M = \text{Ru}$, Rh ; and dimerization of metalloporphyrin occurs if $M = \text{Fe}$. This is due to the oxygen contained in the water (all syntheses were performed without deaeration), and the water itself as a reducing agent.

With Mg , Zn and Cd , contrary to the above-mentioned metals, the coordination process (2) is reversible and affected distinctly by the pH of the solution. Thus, in a certain range of pH, an equilibrium makes it possible to separate these metalloporphyrins; in the other range of pH, a demetalation process occurs. The suitable pH values are above 2 for Zn and Mg , and above 7 in case of Cd .

According to eqn. (5) the reaction of dimerization can occur only in an alkaline medium [10, 27, 28]. Among the metalloporphyrins we have studied, only iron(III) porphyrinate exhibits the ability of dimerization. It was possible that the final product of synthesis was in the form of iron(II) or iron(III), or in the form of a dimer. In order to distinguish the form of product for the respective absorption spectra (Fig. 3a), the solution was alkalinized up to pH 11 (Fig. 3b) and treated with ascorbic acid (Fig. 3c). The absorption band with the maximum at about 394 nm (acidic solution, pH = 4) corresponds to iron(III) porphyrinate. At higher pH, this peak disappears and another with the maximum at $\lambda = 416$ nm is formed. This can be assigned to the

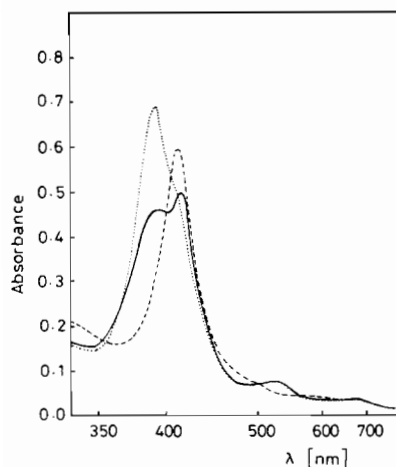


Fig. 3. Absorption spectra: (a) 7.1×10^{-6} M $(\text{TEAPFe})_2\text{O}$ in H_2O at pH 4 (·····); (b) after alkalization up to pH 11 (-·-·-·); (c) after reduction with ascorbic acid (—).

dimeric form $(\text{TEAPFe})_2\text{O}$. For the reduced form of the porphyrinate, a maximum at $\lambda = 420$ nm occurs. Similar to the results that Forshey *et al.* obtained for $\text{TMPyFe}(\text{OH})$ [28], the transition of monomer to dimer was observed in this study at pH 5.

The only conclusion which can be drawn on the basis of visible spectroscopy is that iron(III) porphyrinate was a product of the synthesis. It does not answer the question of whether the complex exists in the form of a monomer or dimer. An explanation of this could be found by applying of IR spectroscopy. Figure 4 shows the IR spectra of the metallo-

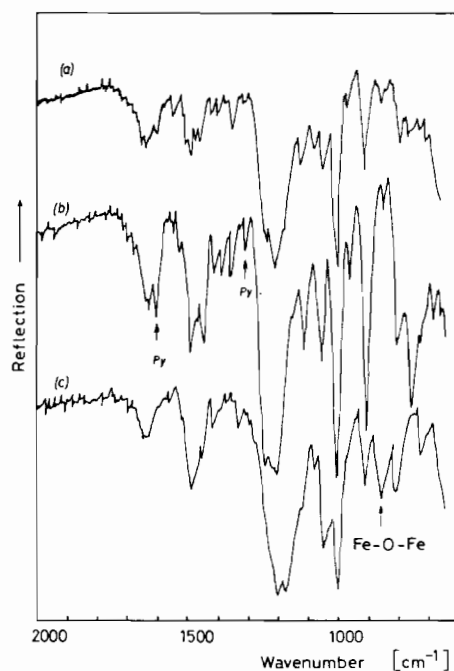


Fig. 4. ATR IR spectra (on KRS-5): (a) $\text{TEAPCo}(\text{OH})$; (b) $\text{TEAPRu}(\text{Py})_2$; (c) $(\text{TEAPFe})_2\text{O}$.

porphyrins of $\text{Co}(\text{III})$, $\text{Ru}(\text{II})$, $\text{Fe}(\text{III})$, respectively. All these spectra contain the same bands except 855 , 1310 and 1610 cm^{-1} . The presence of the band at 855 cm^{-1} was found only in the case of the iron(III) complex (Fig. 4c). This band was detected earlier when the metalloporphyrin contained the bridge of $\text{Fe}-\text{O}-\text{Fe}$ [27, 29]. The bands at 1310 and 1610 cm^{-1} are characteristic of porphyrinates coordinated with pyridine molecules [22]. The bands were detected for the $\text{Ru}(\text{II})$ complex (Fig. 4b). The presence of the above mentioned bands confirm, the saturation efficacy of additional coordination sites by pyridine molecules in ruthenium(II) porphyrinate in the proposed method.

Conclusions

The modified method of preparation presented in this study allows the formation of porphyrin complexes of all transition metals which are water soluble in the whole range of pH values. Porphyrinates of Zn, Mg, Cd, Ni, Ru, Rh and Ag are in form M(II); in case of Fe, Mn and Co, the obtained form of compound is M(III); the form is M(IV) in case of Sn. Iron(III) porphyrinate forms the μ -oxo iron porphyrin dimer.

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