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NEW "AMPHOTERIC ION TYPE" WATER-SOLUBLE PORPHINES AS A SPECTROPHOTOMETRIC REAGENT

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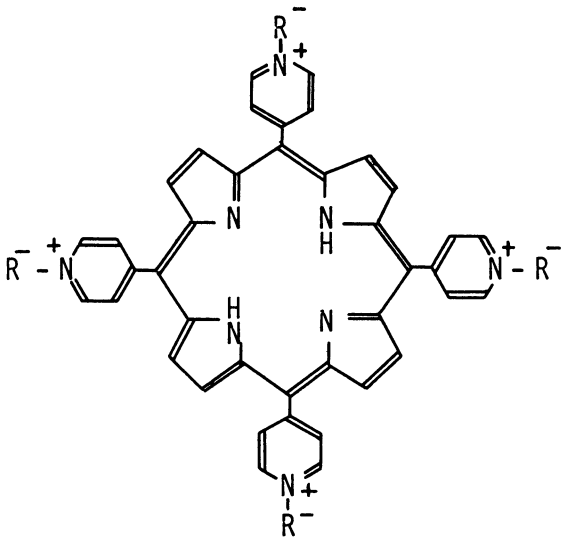
Three kinds of new water-soluble porphines with amphoteric groups were synthesized as highly sensitive spectrophotometric reagents for metal ions. Among them, tetrakis(1-pyridinio-2-sulfoethyl)porphine was a promising reagent because it did not show any adsorption on the surface of glassware over the pH range of 2.0 – 12.4, or any aggregation over its concentration range up to 10^{-4} mol dm^{-3} at the pH range of 0.5 – 13.0.

Porphyrins and their metal complexes have been extensively studied in the biological and other fields of chemistry, and the synthesis of porphines having a new function has become increasingly important. Recently, analytical application of water-soluble porphines as highly sensitive spectrophotometric reagents for metal ions has been demonstrated by using the Soret band (ε = 2 – 6 x 10^5 mol^{-1} dm^3 cm^{-1}, at 400 – 500 nm).[1] However, $\alpha,\beta,\gamma,\delta$-tetrakis-(1-methylpyridinium-4-yl)porphine (TMPyP) and other conventional cationic porphines, were adsorbed on the surface of glassware in neutral or basic aqueous solutions to give a large error in the absorbance measurement. Further,



T(1-PC)P : R^-=-CH_2COO^-

T(1-PH)P : R^-=-$CH_2CH_2O^-$

T(1-PS)P : R^-=-$CH_2CH_2SO_3^-$

Fig. 1. Structure of "amphoteric ion type" porphines (H_2L).

the use of anionic porphines which have sulfophenyl or carboxyphenyl groups was restricted owing to the aggregation reaction under strongly acidic conditions and/or at higher reagent concentration. These characteristics of the porphines may be largely attributed to an electrostatic interaction of cationic porphines with negatively charged glass surface or to a hydrophobic mutual interaction of protonated form of anionic porphines, respectively. Therefore, it is expected that the error caused by these interactions could be avoided by introduction of "amphoteric ion type" functional groups, which have positive and negative charges simultaneously (see Fig.1) into the peripheral moiety of the porphine. Based on this idea, three kinds of new water-soluble porphines were synthesized; α,β,γ,δ-tetrakis(1-pyridinio-2-carboxymethyl)porphine {T(1-PC)P}, tetrakis(1-pyridinio-2-hydroxyethyl)porphine {T(1-PH)P}, and tetrakis(1-pyridinio-2-sulfoethyl)porphine {T(1-PS)P} (Fig.1).

Synthesis: Starting material, α,β,γ,δ-tetrapyridylporphine (TPyP), was synthesized according to the method proposed by Adler et al.[2] T(1-PC)P, T(1-PH)P, and T(1-PS)P were synthesized by refluxing TPyP (0.2 g) with sodium chloroacetate (6.0 g) for 5 h in acetic acid (50 cm^3), with 2-bromoethylenehydrin (5 cm^3) for 10 h in DMF (50 cm^3), and with sodium 2-bromoethane sulfate (7.0 g) for 10 h in DMF (50 cm^3), respectively. The products were purified by column chromatography (activated alumina) and recrystallization. The products, which gave one spot on TLC, were identified by visible spectra (Table 2), infrared spectra, and elemental analysis [T(1-PC)P; Found: C, 43.20; H, 2.95; N, 8.38%. Calcd for $C_{48}H_{34}O_8N_8(ClO_4)_4$: C, 42.80; H, 2.52; N, 8.30%. T(1-PH)P: Found: C, 51.53; H, 4.12; N, 10.02%. Calcd for $C_{48}H_{46}O_4N_8Br_4$: C, 52.33; H, 4.36; N, 12.37%. T(1-PS)P: Found: C, 38.50; H, 3.27; N, 7.69; S, 8.64%. Calcd for $C_{48}H_{42}O_{12}N_8S_4Br_4Na_4$; C, 39.40; H, 2.87; N, 7.66; S, 8.77%.].

These porphines are highly soluble in water and did not show any aggregation over their concentration range of 10^{-7} – 10^{-4} mol dm^{-3} and over the pH range of 0.5 – 13.0. The adsorption of TMPyP and the new porphines on the glass surface was examined (Table 1). The experimental procedure is as follows: 1 cm^3 of 1×10^{-4} mol dm^{-3} porphine was taken into a 25 cm^3 volumetric flask, and pH was adjusted with HNO_3, KH_2PO_4-NaOH, and NaOH solutions. The mixture was diluted

Table 1. Adsorption of free porphines on the glass wall of volumetric flask

Porphine[a]	Weight percentage of adsorbed porphines		
	pH 2.0	pH 6.9	pH 12.4
TMPyP	N.D.[b]	6.90	3.60
T(1-PH)P	N.D.	3.27	1.64
T(1-PC)P	N.D.	2.51	N.D.
T(1-PS)P	N.D.	N.D.	N.D.

a) $[Porphine]_{Total} = 4 \times 10^{-6}$ mol dm^{-3}.

b) N.D. : Not detected (less than 0.50 wt%).

Table 2. Absorption spectra and acid dissociation constants of porphines

Porphine	$\frac{\lambda_{max}}{nm}$ a), $\left(\frac{\varepsilon}{10^4\ mol^{-1}\ dm^3\ cm^{-1}}\right)$ b)								Acid dissociation constants c)		
	H_2L (pH 9.3)					H_4L^{2+} (pH 0.5)					
	Soret	I	II	III	IV	Soret	I	II	pK_{a4}	pK_{a3}	pK_{a2}
T(1-PC)P	422 (20.5)	518 (1.38)	555 (0.64)	585 (0.68)	640 (0.26)	442 (24.7)	590 (1.28)	636 (1.51)	0.83	1.84	13.22
T(1-PH)P	423 (19.7)	517 (1.34)	554 (0.55)	583 (0.60)	640 (0.17)	444 (22.4)	591 (0.81)	637 (1.00)	0.77	1.70	13.47
T(1-PS)P	423 (19.8)	518 (1.50)	555 (0.67)	583 (0.68)	641 (0.21)	446 (25.1)	592 (1.08)	638 (1.01)	1.01	2.02	13.41
TMPyP d)	423 (26.0)	518 (1.80)	556 (0.78)	586 (1.02)	636 (0.43)	444 (32.4)	591 (1.65)	640 (1.78)	0.80	2.06	12.9

a) I - IV indicate the λmax at visible region.

b) ε ; Molar absorption coefficient.

c) $H_4L^{2+} \overset{pK_{a4}}{\rightleftharpoons} H_3L^{+} \overset{pK_{a3}}{\rightleftharpoons} H_2L \overset{pK_{a2}}{\rightleftharpoons} HL^{-}$ ($pK_{an} = -\log [K_{an} / mol\ dm^{-3}]$, $K_{an} = [H_{n-1}L^{(n-3)+}][H_nL^{(n-2)+}]^{-1} a_{H^+}$), determined by spectrophotometric method, at I=0.1 mol dm^{-3} ($NaNO_3$), at 20 °C. These protons are on the nitrogen atoms of the porphine ring.

d) Ref. 3.

to the mark with water. After standing for 15 min, the solution was discarded and the volumetric flask was washed with two 10 cm^3 portions of water. The color of porphine could not be detected in the second washings. Five cm^3 of 1 mol dm^{-3} nitric acid solution was added to the flask and the adsorbed porphine was desorbed from the glass surface. The acid solution was transferred into another 10 cm^3 volumetric flask and was diluted to the mark with water. The absorbance of the solution was measured at the Soret band.

The amounts of the porphine adsorbed on the glass surface decreased in the order of TMPyP $\gg$ T(1-PH)P > T(1-PC)P > T(1-PS)P. Especially, T(1-PS)P did not show any adsorption on the glass surface over the pH range of 2.0 – 12.4.

Spectral data and acid dissociation constants of the new porphines are summarized in Table 2. They are comparable to those of TMPyP, shown in the last line of Table 2.

These porphines formed metal complexes with Co^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Pd^{2+}, and Zn^{2+} The stoichiometric metal:ligand ratio of these complexes deduced from the molar ratio method was 1:1. The Soret band spectra of these metal complexes are shown in Table 3. One of the promising features of T(1-PS)P

Table 3. Soret band absorption spectra of metal-porphine complexes

Metal ion	$\frac{\lambda_{max}}{nm}$, $\left(\frac{\varepsilon}{10^4\ mol^{-1}\ dm^3\ cm^{-1}}\right)$			
	T(1-PC)P	T(1-PH)P	T(1-PS)P	TMPyP
Cd(II)	443 (17.9)	449 (16.1)	446 (18.1)	448 (23.0)
Co(II)	436 (10.5)	439 (13.2)	437 (15.9)	436 (13.7)
Cu(II)	427 (19.7)	426 (18.1)	423 (18.1)	425 (21.0)
Pb(II)	475 (17.6)	476 (16.4)	476 (15.6)	476 (17.9)
Pd(II)	418 (18.6)	417 (16.6)	422 (18.1)	418 (19.0)
Zn(II)	427 (19.7)	438 (18.3)	435 (20.1)	437 (22.8)

is that its rate of complxation with several kinds of metal ions was larger than that of anionic water-soluble porphines.[1] For example, Cd^{2+}, Pb^{2+}, and Zn^{2+} complexes were quantitatively formed within 1 min at room temperature under appropriate conditions ($[metal\ ion]_T=4 \times 10^{-6}$ mol dm^{-3}, $[T(1-PS)P]_T=4 \times 10^{-6}$ mol dm^{-3}, pH regions: pH 9.5 – 12.5 for CdL, pH 8.0 – 12.5 for PbL, pH 9.0 – 10.5 for ZnL).

These results show that the introduction of amphoteric functional groups successfully improve aggregation and adsorption characteristics of TMPyP, without any marked change in the other analytically important properties. Thus, the amphoteric ion type porphines can be used as excellent spectrophotometric reagents for metal ions, as well as the reagents for fluorimetry[4] and for high performance liquid chromatography[5] of metal ions.

References

1) T.Yotsuyanagi, Kagaku, 35, 233(1980).
2) A.D.Adler, F.R.Longo, F.D.Finarelli, J.Goldmacher, J.Assour, and K.Korsakoff, J.Org.Chem., 32, 476(1968).
3) P.Hambright and P.B.Chock, J.Am.Chem.Soc., 96, 3123(1974).
4) S.Igarashi, T.Yotsuyanagi, and K.Aomura, Nippon Kagaku Kaishi, 1981, 60.
5) S.Igarashi, T.Hashimoto, Y.Matsumoto, and T.Yotsuyanagi, Bunseki Kagaku, 32, 591(1983).

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