Spectrophotometric Study on the Complexation of Silver Ions with 5,10,15,20-Tetrakis(1-methylpyridinio)porphines

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Three cationic porphyrins, 5,10,15,20-tetrakis(1-methyl-2-pyridinio)porphine [T(2-MPy)P], 5,10,15,20-tetrakis(1-methyl-3-pyridinio)porphine [T(3-MPy)P] and 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphine [T(4-MPy)P], react rapidly and quantitatively with silver(I) to form yellow complexes in alkaline solutions of pH 9.6–12.0, which are oxidized to the corresponding red silver(II) complexes by dissolved oxygen at room temperature. The silver(II) complexes formed were stable and remained unchanged for at least 2 h. The composition of the silver(II) complex was determined to be 1:1 (metal:ligand) by both the continuous variation method and the molar ratio method. Highly sensitive spectrophotometric methods for the determination of the trace amounts of silver have been developed. The apparent molar absorptivities of the silver(II) complexes of T(2-MPy)P, T(3-MPy)P and T(4-MPy)P were 3.00×10^5 , 3.36×10^5 and $2.30 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$, respectively. Cadmium(II), cobalt(II), copper(II), mercury(II), manganese(II), zinc(II), halogenides, thiocyanide and cyanide interfered with the silver determination.

Keywords Silver, 5,10,15,20-tetrakis(1-methylpyridinio)porphines, porphyrin, spectrophotometry

Cationic porphyrins, 5,10,15,20-tetrakis(1-methyl-3-pyridinio)porphine [T(3-MPy)P] and 5,10,15,20-tetrakis(1-methyl-4-pyridinio)porphine [T(4-MPy)P], have the characteristics that they do not aggregate even in strongly acidic solutions and/or at higher concentrations where anionic porphyrins having sulfophenyl or carboxyphenyl groups aggregate and that they usually react more rapidly with metal ions to form complexes than the anionic porphyrins. These cationic porphyrins have therefore already been used for the spectrophotometric determination of micro amounts of copper¹⁻⁸, zinc^{9,10} and cadmium¹¹, although they have a disadvantage in that they and their metal complexes are adsorbed on the surfaces of glassware in neutral or alkaline solutions, causing errors in absorbance measurements. However, as for 5,10,15,20-tetrakis(1-methyl-2-pyridinio)porphine [T(2-MPy)P], a position-isomer of the above mentioned cationic porphyrins, it was already synthesized¹², though its analytical application has not yet been studied.

On the other hand, during the course of a continued investigation of the analytical application of these cationic porphyrins including T(2-MPy)P, we have found that these porphyrins react rapidly with silver(I) to form complexes which are easily oxidized to the

corresponding stable silver(II) complexes at room temperature. The complexation reactions have therefore been studied in detail. In this paper the results are

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described and the applicability of these porphyrins to the spectrophotometric determination of silver is discussed. The structures of three porphyrins studied in this work are shown in (I).

Experimental

Reagents

All reagents used were of analytical-reagent grade unless stated otherwise. All solutions were prepared with distilled, de-ionized water.

T(2-MPy)P, T(3-MPy)P and T(4-MPy)P solutions, 1×10^{-4} M. Prepared by dissolving the required mass of each porphyrin tosylate in water. T(2-MPy)P, T(3-MPy)P and T(4-MPy)P tosylates were synthesized and purified by a method described in the literature.^{12,13}

Standard silver(I) solution, 1.0×10^{-2} M. Prepared by dissolving 170 mg of silver nitrate (dried at 110°C) in 50 ml of 0.1 M nitric acid and diluting to 100 ml with water. Working solutions were prepared by dilution of this solution with water.

Lead(II) solution, 3×10^{-4} M. Prepared by dissolving 0.1 g of lead nitrate in 1 litre of water, sufficient nitric acid to give a pH of ca. 2 being added.

Procedures

Procedure with T(3-MPy)P (Procedure A). To an aliquot containing up to 8 μg of silver(I) in a 25-ml calibrated flask, add 2 ml of 1×10^{-4} M T(3-MPy)P solution and 1 ml of a 0.1-M sodium hydroxide solution. After allowing to stand for about 5 min, add 1 ml of a 3×10^{-4} M lead(II) solution and 5 ml of a 1.5-M sodium sulfate solution and dilute to the mark with water. Measure the absorbance of the resultant colored solution at 425.5 nm against a reagent blank prepared under the same conditions using 1-cm cells.

Procedure with T(2-MPy)P (Procedure B). Place an aliquot containing up to 9 μg of silver(I) in a 25-ml calibrated flask and prepare the colored solution in a similar way to that in procedure A, except for using 2 ml of a 1×10^{-4} M T(2-MPy)P solution instead of a T(3-MPy)P solution. Measure the absorbance at 422 nm.

Procedure with T(4-MPy)P (Procedure C). Place an aliquot containing up to 12 μg of silver(I) in a 25-ml calibrated flask and prepare the colored solution in a similar way to that in procedure A, except for using 2 ml of a 1×10^{-4} M T(4-MPy)P solution instead of a T(3-MPy)P solution. Measure the absorbance at 430.5 nm.

Results and Discussion

Acid dissociation constants of the porphyrins

As is evident from the structure of the porphyrins, at least five species (H_4L^{6+} , H_3L^{5+} , H_2L^{4+} , HL^{3+} and L^{2+}) are involved in their acid-base equilibria, the probable

Table 1 Acid dissociation constants of porphyrins

Porphyrin	Acid dissociation constants	
	$\text{p}K_{\text{a}2}$	$\text{p}K_{\text{a}3}$
T(2-MPy)P		11.7 ($\mu=0.1$)
T(3-MPy)P	2.3 ($\mu=1$) ^a	13.4 ($\mu=0.5$)
T(4-MPy)P	2.1 ($\mu=1$) ^a	12.9 ($\mu=0.5$) ^b

a. ref. 14. b. ref. 15.

equilibria being as follows:

where L denotes the undissociable part of the porphyrin and $K_{\text{a}1}$, $K_{\text{a}2}$, $K_{\text{a}3}$ and $K_{\text{a}4}$ are the acid dissociation constants. Among these constants the value of $K_{\text{a}3}$ of T(2-MPy)P and T(3-MPy)P were determined spectrophotometrically at $25 \pm 0.1^\circ\text{C}$ in this work. The result is shown in Table 1 together with the values of $K_{\text{a}2}$ and $K_{\text{a}3}$ of T(3-MPy)P and T(4-MPy)P reported already. From Table 1 it can be seen that the basicity of these three porphyrins decreases along the sequence T(3-MPy)P > T(4-MPy)P > T(2-MPy)P, the basicity of T(2-MPy)P being the smallest.

Complexation reactions

A preliminary experiment revealed that silver(I) reacts with T(2-MPy)P, T(3-MPy)P and T(4-MPy)P to form yellow silver(I) complexes in alkaline solutions of pH above 9, and they are gradually oxidized to red silver(II) complexes by dissolved oxygen. Under optimum conditions the formation of the silver(I) complexes was almost instantaneous, oxidation proceeded relatively rapidly and the formation of the silver(II) complexes came to completion within several minutes at room temperature, as shown in Fig. 1. This is very favorable for the determination of silver with these porphyrins.

The changes in color and spectra, shown here, in the oxidation of the silver complexes are very similar to those in the oxidation of the silver-5,10,15,20-tetra-phenylporphine complex from the green disilver monovalent complex to the reddish-orange monosilver divalent complex.¹⁶

Absorption spectra

Absorption spectra of T(2-MPy)P, T(3-MPy)P, T(4-MPy)P and their silver(II) and lead(II) complexes in the Soret region are shown in Fig. 2, absorption maximum wavelengths of the silver(II) complexes being summarized in Table 2 along with their apparent molar absorptivities. From Fig. 2 it is found that whichever porphyrin is used, the Soret band of the silver(II) complex overlaps remarkably with that of the porphyrin itself around pH 11.4, where the formation of the silver(II) complex proceeds rapidly and smoothly.

Fig. 1 Spectral changes of Ag-T(2-MPy)P, -T(3-MPy)P and -T(4-MPy)P complexes with the passage of time. Ag, 1.9×10^{-5} M; T(2-MPy)P, T(3-MPy)P, T(4-MPy)P, 5.1×10^{-6} M; pH, 11.5; reference, water. (a), T(2-MPy)P complex; (b), T(3-MPy)P complex; (c), T(4-MPy)P complex. Arrows indicate the trend of spectral changes with the passage of time.

Fig. 2 Absorption spectra of T(2-MPy)P, T(3-MPy)P, T(4-MPy)P and their silver(II) and lead(II) complexes. Ag, 3.8×10^{-6} M; T(2-MPy)P, T(3-MPy)P, T(4-MPy)P, 2.2×10^{-6} M; Pb, 4.7×10^{-6} M; Na_2SO_4 , 0.3 M; pH, 11.4; reference, water. (a), T(2-MPy)P and its complexes; (b), T(3-MPy)P and its complexes; (c), T(4-MPy)P and its complexes. A, Ag(II) complex; B, Pb(II) complex; C, porphyrin alone ($\text{H}_2\text{L}^{4+} + \text{HL}^{3+}$).

Table 2 Absorption maxima and apparent molar absorptivities (ϵ) of silver(II) complexes, equations of calibration curves and optimum pH ranges for the silver determination

Procedure using	In presence of	
	0.3 M Na ₂ SO ₄	0.4 M NaNO ₃
T(2-MPy)P	$\lambda_{\max}=422$ nm Ag(ppb)=360.4 $\epsilon=3.00 \times 10^5$ Optimum pH range: 9.6–12.5	$\lambda_{\max}=423.5$ nm Ag(ppb)=367.4 $\epsilon=2.94 \times 10^5$
T(3-MPy)P	$\lambda_{\max}=425.5$ nm Ag(ppb)=321.4 $\epsilon=3.36 \times 10^5$ Optimum pH range: 9.2–12.4	$\lambda_{\max}=427.5$ nm Ag(ppb)=336.4 $\epsilon=3.21 \times 10^5$
T(4-MPy)P	$\lambda_{\max}=430.5$ nm Ag(ppb)=470.4 $\epsilon=2.30 \times 10^5$ Optimum pH range: 9.3–12.0	$\lambda_{\max}=431$ nm Ag(ppb)=533.4 $\epsilon=2.02 \times 10^5$

A denotes absorbance.

However, the Soret band of the lead(II) complex is well separated from those of the porphyrin and its silver(II) complex. This indicates that when the absorbance of the Soret band of the silver(II) complex is measured for the determination of silver, the porphyrin which exists in excess interferes strongly; however, when the absorbance measurements were carried out after the conversion of the excess porphyrin into its lead(II) complex, such a spectral interference could be completely removed. In fact, this expectation could be realized by adding lead(II) after the formation of the silver(II) complex was completed, since lead(II) forms the complex rapidly with excess porphyrin of around pH 11.4.

Another fact derived from Fig. 2 and Table 2 is that the molar absorptivity of the silver(II) complex is highest when T(3-MPy)P was used and decreases along the sequence T(3-MPy)P complex > T(2-MPy)P complex > T(4-MPy)P complex. This suggests that the highest sensitivity is obtained in the determination of silver when T(3-MPy)P is used as a color-producing reagent.

Effect of pH

The effect of pH on the formation of the silver(II) complexes was examined. The optimum pH ranges for the complexations where constant and maximum absorbances are obtained are summarized in Table 2, the effect of pH on the formation of the silver(II)-T(3-MPy)P complex being shown in Fig. 3 as an example. The complex formations are found to be performed quantitatively over relatively wide pH ranges.

Effect of porphyrin concentration

The effect of the porphyrin concentration was examined at pH 11.4 by varying the concentration of T(2-MPy)P, T(3-MPy)P or T(4-MPy)P and keeping the silver(I) concentration at 245 ppb. The results revealed

Fig. 3 Effect of pH on the formation of the silver(II)-T(3-MPy)P complex. Ag, 245 ppb (2.27×10^{-6} M); T(3-MPy)P, 5.1×10^{-6} M; Pb, 9.3×10^{-6} M; Na₂SO₄, 0.3 M; reference, reagent blank.

that a constant and maximum absorbance is obtained in every case, provided that more than about a 1.5-fold molar excess of the porphyrin is added, and that the excess porphyrin does not interfere with the silver determination, since it has been converted to the lead(II) complex before absorbance measurements.

Stability of the complexes

Both of the silver(II) and lead(II) complexes of T(2-MPy)P, T(3-MPy)P and T(4-MPy)P formed were stable and remained unchanged for at least 2 h under the recommended conditions.

Composition of the complexes

The compositions of the silver(II) complexes of T(2-MPy)P, T(3-MPy)P and T(4-MPy)P were determined by the continuous-variation method and the molar-ratio method. The results revealed the formation of a 1:1 (metal:ligand) complex in every case.

Suppression of adsorption

As has already been pointed out by us, in general, cationic porphyrins and their metal complexes are adsorbed on the inner surfaces of glassware because of an electrostatic interaction between positive charge on the substituents at the *meso*-position of the porphine ring and negative charge on the glass surface.¹¹ This kind of adsorption was also observed in the work, though it could be almost completely suppressed by adding sodium sulfate or nitrate sufficient to give a concentration of more than about 0.2 M in the final solution.

By the way, in general, the Soret band of the metal-porphyrin complex is known to shift gradually and slightly upon increasing the concentration of a salt added as an adsorption suppressor.¹¹ In fact, this phenomenon was observed in this work when sodium nitrate was added, although no appreciable shift in the wavelength was observed when sodium sulfate was

Table 3 Influence of foreign ions

Ion	Tolerance limit
Ca(II), ^a Mg(II) ^a	1000 µg
Al(III)	500 µg
Ni(II), Pt(IV) ^a	100 µg
Au(III), Fe(II), V(V)	50 µg
Cr(III), Cr(VI), Fe(III), Pb(II), Pd(II), V(IV)	10 µg
Hg(II)	4 µg
Cd(II), Co(II), Cu(II), Mn(II), Zn(II)	<4 µg
NO ₃ ⁻ , ^a SO ₄ ²⁻ ^a	100 mg
Cl ⁻	10 mg
ClO ₄ ⁻	5 mg
Br ⁻ , I ⁻ , CN ⁻ , SCN ⁻	<100 µg

Ag(I) taken, 3.74 µg; allowable error, ±3%.

a. Maximum tested.

added. In addition, the oxidation of the silver(I) complex to the silver(II) complex was somewhat slowed down upon increasing the concentration of the salt. Hence, it was recommended that 0.2–0.5 M (in the final solution) of sodium sulfate is added as an adsorption suppressor.

Conformance with Beer's law

Plots of the absorbance *versus* the silver concentration in the three procedure were all linear and passed through the origin. The equation of the lines obtained by a least-squares treatment and the apparent molar absorptivities calculated from these equation are summarized in Table 2 together with the optimum pH ranges for the silver determination. The highest sensitivity was found to be obtained when T(3-MPy)P was used as a color-producing reagent.

Influence of other ions

Solutions containing a fixed amount of silver(I) and various amounts of other ions were prepared and the developed procedures were followed. An error of less than ±3% in the absorbance reading was considered to be tolerable. Table 3 shows the influence of other ions when T(3-MPy)P was used as a color-producing reagent. Similar results to that shown in Table 3 were obtained when the other porphyrins were used. Metal ions including cadmium(II), cobalt(II), copper(II), mercury(II), manganese(II) and zinc(II) interfered with the silver determination because of the complex formation with the porphyrins. Anions such as bromide, iodide, cyanide and thiocyanide also interfered because of complex formations with silver(I). Thus, the suppression and/or removal of these interferences by the addition of various masking agents was examined; however, no effective and suitable masking agent was

found, in spite of eager trials. Therefore, prior separation of silver(I) from these interferents is necessary in order to apply the developed methods to analyses of real samples.

In conclusion, the complexation of three cationic porphyrins with silver ions has been studied spectrophotometrically. On the basis of the results, three highly sensitive spectrophotometric methods for the determination of silver have been developed. These methods have the highest sensitivity among those which have ever been reported, but are subject to interference from many other ions; this interference could not be removed. Regrettably, the practicability of the methods, therefore, is not high. However, the interference by anions suggests possibility of a highly sensitive indirect spectrophotometric determination of the anions. This was an unexpected but useful finding in this work. Studies concerning this are now in progress.

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