crease in the strength of the Sn-O bonds. On the other hand, the frequency variation within the series of $Sn(acac)_2X_2$ complexes could result from the variation in mass of the SnX_2 group to which the oxygens are attached. (It is pertinent to note that the frequencies of the 450-cm^{-1} band ($I < Br < Cl < F$) do not correlate with the rates of configurational rearrangement ($Cl < Br < I < F$)). In any case, the halogen-substituent effect does support assignment of the 450-cm^{-1} band to a Sn-O stretching mode rather than an acac ligand vibration. A similar halogen substituent effect on the band occurring at 598-582 cm^{-1} suggests that this normal mode also involves some Sn-O stretching. The frequencies of the 688- and 420-cm^{-1} bands are less dependent on the halogen; ^{18}O- and metal-labeling studies of related compounds suggest that these bands arise from ring deformations involving substantial motion of the oxygens but relatively little metal-oxygen stretching.[45-47]

The assignment of metal-halogen vibrations is evident from a comparison of the spectra in the region below 600 cm^{-1} (see Figure 4 and Table IX). For the cis isomer, both symmetric and asymmetric Sn-X stretching modes are infrared active. These are observed in the spectrum of $Sn(acac)_2F_2$ as unique bands of comparable intensity at 586 and 571 cm^{-1} in solution and at 581 and 563 cm^{-1} in the solid state. In agreement with Douek, *et al.*,[16] we assign the unique, strong bands at 344, 262, and 180 cm^{-1} to Sn-Cl, Sn-Br, and Sn-I stretching modes, respectively. The symmetric and asymmetric components are split by 11 cm^{-1} in the spectrum of solid $Sn(acac)_2I_2$; in general, however, ν_s(Sn-X) and ν_{as}(Sn-X) are not resolved in our spectra when X = Cl, Br, or I. Cox, *et al.*,[20] assigned bands at 334 and 264 cm^{-1} to Sn-Cl stretching in the dichloride, but the latter assignment seems unlikely in view of the small splitting (15-18 cm^{-1}) between the symmetric and asymmetric modes in the difluoride. We believe that the broad band at 344 cm^{-1} (334 cm^{-1} in the solid) results from overlap of the two Sn-Cl stretching modes. Douek, *et al.*,[16] claimed that the second ν(Sn-Cl) can be seen as a shoulder at 338 cm^{-1}, which would make the splitting about 7 cm^{-1}.

The X-Sn-X bending modes, $\nu_5(T_{2g})$, of SnF_6^{2-} and $SnCl_6^{2-}$ have been observed at 252[48] and 158 cm^{-1},[49] respectively. On this basis we assign the strong band of $Sn(acac)_2F_2$ at 247 cm^{-1} to the F-Sn-F bending mode and tentatively assign the 142-cm^{-1} band of $Sn(acac)_2Cl_2$ to the Cl-Sn-Cl bending mode.

The nearly exact correspondence of the solution and solid-state spectra of the $Sn(acac)_2X_2$ complexes indicates that the stereochemistry is cis in the solid state as well as in solution. This is supported by observation of two Sn-X stretching bands in the solid-state spectra of $Sn(acac)_2F_2$ and $Sn(acac)_2I_2$ and by a recent single-crystal X-ray study of $Sn(acac)_2Cl_2$.[50]

Acknowledgments. Support of this research by National Science Foundation Grants GP-16280 and GP-30691X is gratefully acknowledged. We also thank Drs. T. L. Brown and J. A. Ladd for the computer program which was used in the line shape calculations.

Registry No. $Sn(acac)_2F_2$, 25426-91-9; $Sn(acac)_2Cl_2$, 16919-65-6; $Sn(acac)_2Br_2$, 16919-66-7; $Sn(acac)_2I_2$, 16919-67-8; tin(IV) fluoride, 7783-62-2; acetylacetone, 123-54-6.

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Aggregation of Nickel(II), Copper(II), and Zinc(II) Derivatives of Water-Soluble Porphyrins

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The solution properties of the nickel(II), copper(II), and zinc(II) derivatives of tetracarboxyphenylporphine (TCPP) and tetra(*N*-methylpyridyl)porphine (TMPyP) have been investigated. At $\mu = 0.1\ M$ and 25°, NiTMPyP, CuTMPyP, ZnTMPyP, and ZnTCPP show no tendency to aggregate. However, under these conditions NiTCPP and CuTCPP dimerize with concentration equilibrium constants of 1.57×10^5 and $1.69 \times 10^5\ M^{-1}$, respectively. The kinetics of the process $2MTCPP \rightleftarrows (MTCPP)_2$ (k_{22}, k_{-22}) have been investigated *via* the temperature-jump technique. For NiTCPP, $k_{22} = 6.2 \times 10^7\ M^{-1}\ sec^{-1}$ and $k_{-22} = 4.0 \times 10^2\ sec^{-1}$; for CuTCPP, $k_{22} = 4.5 \times 10^7\ M^{-1}\ sec^{-1}$ and $k_{-22} = 2.7 \times 10^2\ sec^{-1}$.

Introduction

The chemical and physical properties of metalloporphyrins continue to attract considerable interest because of the vital role some of these species play in biological processes. The porphyrin ligand has a profound influence on the kinetic and thermodynamic properties of the metal center with respect to ternary complex formation and oxidation-reduction behavior.[3] Recent studies have shown that some meso-substituted porphyrins dimerize in aqueous solution;[4,5] the tendency of porphyrins to aggregate is also of considerable biological significance.[6,7]

The properties of water-soluble porphyrins of the meso-substituted variety are dependent on the charge type of the periphery of the molecule. Porphyrins having negative

(1) NSF Undergraduate Research Program participant, summer 1972.

(2) In partial fulfillment of the B.A. degree at Ithaca College.

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charges at the periphery ($TPPS_3$ and TCPP)[8] are considerably more basic and have much greater tendency to aggregate than those having positive charges at the periphery (TPyP and TMPyP). A combination of spectral and relaxation measurements has proven very useful in determining the extent and rates of aggregation and we have now applied these techniques to metalloporphyrins. We have studied the aggregation tendencies of the nickel(II), copper(II), and zinc(II) derivatives of TMPyP and TCPP to determine the influence of the metal center on the kinetics of formation and stability of aggregates.

Experimental Section

Materials. TCPP was synthesized and purified by a method described in the literature.[4,9] The method used for synthesizing TMPyP has been modified slightly from that published earlier.[4] Instead of refluxing TPyP with methyl *p*-toluenesulfonate in DMF overnight, the refluxing was continued for only 1.5 hr. The TMPyP was recovered from hot DMF, washed with acetone, and dried under high vacuum.

The metal derivatives of these porphyrins were prepared in a manner suggested by Adler and coworkers.[10]

NiTMPyP. Excess $NiCl_2 \cdot 6H_2O$ was refluxed with TMPyP in water overnight. The solution was cooled and the metalloporphyrin was precipitated with sodium perchlorate. The crystals were collected, washed with dilute perchloric acid solution, and dried *in vacuo*. *Anal.* Calcd for $C_{44}H_{36}N_8Ni(ClO_4)_4$: C, 46.63; H, 3.20; N, 9.89. Found: C, 46.66; H, 3.32; N, 9.75.

CuTMPyP. $Cu(ClO_4)_2$ was refluxed with TMPyP in water for about 1 hr. The solution was cooled and filtered; the crystals were washed with dilute $HClO_4$ and dried *in vacuo*. *Anal.* Calcd for $C_{44}H_{36}N_8Cu(ClO_4)_4$: C, 46.43; H, 3.19; N, 9.85. Found: C, 46.59; H, 3.35; N, 9.89.

ZnTMPyP. Zinc acetate was refluxed with TPyP obtained from the Mad River Chemical Co., Yellow Springs, Ohio, for 1 hr in DMF. The solution was cooled in an ice bath, and the resulting purple crystals (ZnTPyP) were washed with water to remove excess zinc acetate and then washed with acetone. The crystals were dried under high vacuum and dissolved in DMF, and the solution was refluxed for 1-2 hr with methyl *p*-toluenesulfonate. The recovered purple crystals were washed with acetone; they were extremely soluble in water. *Anal.* Calcd for $C_{72}H_{64}N_8O_{12}S_4Zn$: C, 60.61; H, 4.52; N, 7.85; S, 8.99. Found: C, 60.49; H, 4.65; N, 7.99; S, 8.85.

NiTCPP. Excess $NiCl_2 \cdot 6H_2O$ was refluxed with TCPP in DMF overnight. The mixture was filtered at room temperature and an impure porphyrin material was recovered, washed with acetone, and dried. The product was dissolved in 200 ml of 3 *M* NaOH and 400 ml of ethyl acetate was added. At this point, the porphyrin was in the aqueous layer. About 1 *M* HCl was added until the intensely colored porphyrin was transferred into the organic layer. The organic layer was collected, washed with water, and filtered. The solvent was removed and the product was dried *in vacuo*. *Anal.* Calcd for $C_{48}H_{28}N_4O_8Ni$: C, 68.03; H, 3.33; N, 6.61. Found: C, 67.88; H, 3.51; N, 6.44.

CuTCPP. Cupric chloride was refluxed with TCPP in DMF for about 0.5 hr. The volume of the solution was decreased and acetone was added to precipitate the CuTCPP. The crystals were washed with acetone and dried. *Anal.* Calcd for $C_{48}H_{28}N_4O_8Cu$: C, 66.24; H, 3.47; N, 6.44. Found: C, 66.35; H, 3.52; N, 6.53.

ZnTCPP. Zinc chloride was refluxed with TCPP in DMF for about 1.5 hr. The volume of the solution was decreased to almost dryness and water was added to precipitate ZnTCPP. The result was a thick mass of fine wet ZnTCPP which was lyophilized overnight. *Anal.* Calcd for $C_{48}H_{28}N_4O_8Zn \cdot {}^5/_2H_2O$: C, 64.07; H, 3.67; N, 6.23. Found: C, 63.90; H, 3.70; N, 6.24.

Spectral and Kinetic Studies. All visible spectra were determined on a Cary 14 and relaxation experiments were carried out using a temperature-jump apparatus described elsewhere.[11] Solutions were always freshly prepared and were protected from direct sunlight and fluorescent light. A stream of nitrogen was maintained in the temperature-jump cell compartment, and each relaxation time represents an average of at least three photographic determinations, with the relative error of these measurements at ±15%.

Calculations of the equilibrium and kinetic parameters were carried out on the Ithaca College Univac 70/35 computer. For the equilibrium calculations a general minimization routine, SIMPLEX, was used.[12]

Results

Spectral measurements in aqueous solution in the range 400-700 mμ were carried out for the six metalloporphyrins. The species, CuTMPyP, ZnTMPyP, NiTCPP, CuTCPP, and ZnTCPP, all show typical metalloporphyrin spectra with a very intense absorption at about 400-450 mμ (Soret band) and two other prominent bands at longer wavelength of much lesser intensity. The spectrum of NiTMPyP is unusual in that the Soret region is comprised of two overlapping bands of comparable intensity (λ_{max} ~420, ~440 mμ) as shown in Figure 1. This feature of the NiTMPyP spectrum has been studied extensively[13] and, on the basis of spectral and nmr results, it has been concluded that the two Soret bands arise from an equilibrium in solution between four-coordinate and six- (or possibly five-) coordinate nickel. Evidence points to the band at 420 mμ being due to a four-coordinate nickel species (no axial ligands), while the band at 440 mμ is due to the binding of axial ligands to nickel.

$$NiP + 2H_2O \rightleftarrows NiP(H_2O)_2 \qquad (1)$$

The addition of acetone or acetonitrile promotes the 420-mμ band (NiP) at the expense of the 440-mμ band ($NiP(H_2O)_2$) and a 30% mixture of the organic solvent in water is sufficient to shift the equilibrium entirely to the four-coordinate form.

The aggregation tendencies of all six metalloporphyrins were considered in aqueous solutions and for NiTMPyP, both in water and in a 30% acetone-water mixture. Beer's law experiments were conducted for NiTMPyP, CuTMPyP, and ZnTMPyP at 0.1 *M* ionic strength. For most of the experiments, KNO_3 or KCl was used as the electrolyte but experiments were also conducted in 0.1 *M* NaCl or 0.1 *M* $NaClO_4$. The porphyrin spectra showed no dependence on the nature of the electrolyte and, for each of these three metallo derivatives of TMPyP, the plot of absorbance/cell path length *vs.* porphyrin concentration was linear over a 500-fold concentration range from 10^{-7} to 5×10^{-5} *M*. For NiTMPyP, Beer's law was obeyed both in water and in the mixed-solvent system.

Temperature-jump experiments were attempted at the Soret band and at the major visible band for the tetra(*N*-methylpyridyl)metalloporphyrins. Relaxation experiments have proven quite useful in determining whether a given water-soluble porphyrin aggregates.[4,5,14,15] No measurable relaxation effects were obtained for any of these three metalloporphyrins although, for NiTMPyP, the 8° temperature rise resulted in an appreciable color change. Previous work with aggregating porphyrins has shown that these species give relaxation effects longer than 50 μsec. There-

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[8] Abbreviations used: $TPPS_3$, tetraphenylporphinesulfonate; TCPP, tetracarboxyphenylporphine; TPyP, tetrapyridylporphine; TMPyP, tetra(*N*-methylpyridyl)porphine; TEP IX, tetraethylenediamine derivative of protoporphyrin IX.

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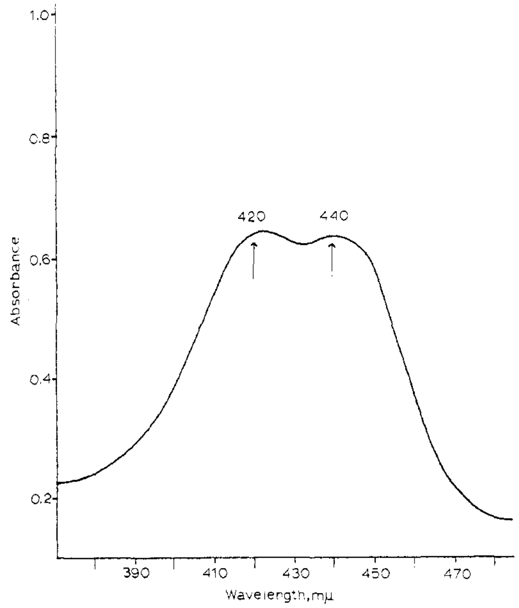

Figure 1. Spectrum of NiTMPyP in water in the Soret region.

fore, the spectral and relaxation experimental results are consistent with the conclusions (i) that none of the porphyrins NiTMPyP (λ_{max} 418 mμ, ϵ 1.49 × 10^5 M^{-1} cm^{-1} in 30% acetone-water), CuTMPyP (λ_{max} 426 mμ, ϵ 2.31 × 10^5 M^{-1} cm^{-1}), nor ZnTMPyP (λ_{max} 437 mμ, ϵ 2.04 × 10^5 M^{-1} cm^{-1}) aggregates appreciably in solution and (ii) that while equilibrium 1 for NiTMPyP is temperature dependent, the relaxation process is too rapid to measure on a conventional temperature-jump instrument.[13]

The spectra of NiTCPP, CuTCPP, and ZnTCPP show one band in the Soret region at ~410, ~410, and 423 mμ, respectively. Unlike the situation for the TMPyP derivatives, the position and intensities of the bands for NiTCPP and CuTCPP are ionic strength dependent. Beer's law experiments, in the *absence of added electrolyte*, were run at 411 mμ for NiTCPP and at 415 mμ for CuTCPP. For both metalloporphyrins, Beer's law was obeyed over an extended concentration range ($2 \times 10^{-7} <$ [NiTCPP] $< 6 \times 10^{-5}$ M and $10^{-7} <$ [CuTCPP] $< 5 \times 10^{-5}$ M) although there was an indication of some deviation for [CuTCPP] $> 2 \times 10^{-5}$ M. We obtain ϵ 2.28 × 10^5 M^{-1} cm^{-1} for NiTCPP and ϵ 3.64 × 10^5 M^{-1} cm^{-1} for CuTCPP. Because of the slight curvature for the copper derivative, we considered this porphyrin in an 80% ethylene glycol-water mixture as well and found no deviation from Beer's law in this solvent system over a 300-fold concentration range. We obtain ϵ 4.02 × 10^5 M^{-1} cm^{-1} at 415 mμ in 0.1 M KNO_3 with 0.001 M Tris as a buffer, pH 7.3 in water.

In aqueous solution, the presence of an electrolyte causes large deviations from Beer's law behavior for NiTCPP and CuTCPP. A plot of absorbance/cell path length *vs.* concentration is shown in Figure 2 for NiTCPP and in Figure 3 for CuTCPP. In both cases, the ionic strength is 0.1 M and the pH is buffered at 7.5 and 6.8, respectively, by 0.001 M Tris. The curvature in the Beer's law plots is interpreted as being due to aggregation of NiTCPP and CuTCPP although a model involving electrolyte bonding to the porphyrin was also considered. Experiments conducted on NiTCPP and CuTCPP are summarized in Table I. At a constant porphyrin concentration, the absorbance was shown to be dependent on the concentration but not the nature of the 1:1 electrolyte used to maintain the ionic strength. Furthermore, it was

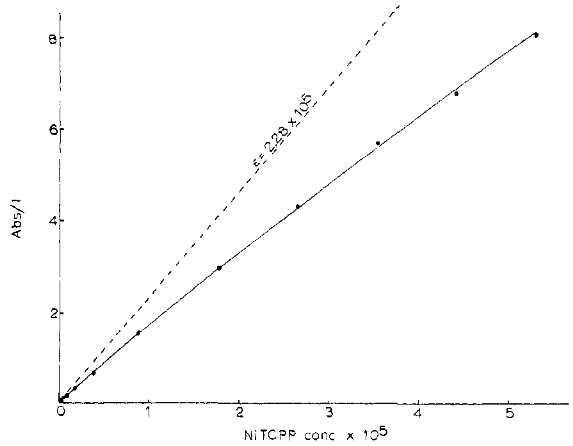

Figure 2. Beer's law experiment for NiTCPP in aqueous solution, pH 7.5, 0.1 M KNO_3 at 411 mμ. The line marked ϵ 2.28 × 10^5 defines Beer's law behavior for NiTCPP. The filled circles represent the experimental data and the theoretical curve is shown which was obtained for a dimerization model with ϵ_D 2.70 × 10^5 M^{-1} cm^{-1} and $K = 1.57 \times 10^5$ M^{-1}

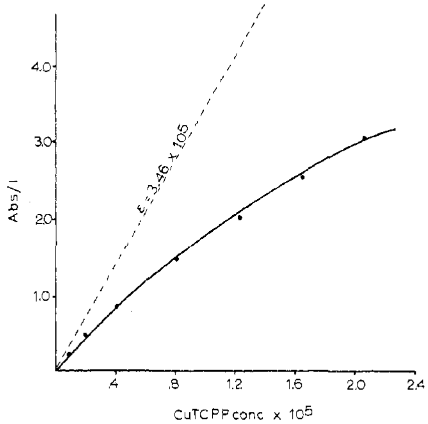

Figure 3. Beer's law experiment for CuTCPP in aqueous solution, pH 6.8, 0.1 M KCl at 415 mμ. The line marked ϵ 3.46 × 10^5 defines Beer's law behavior for CuTCPP. The filled circles represent the experimental data and the theoretical curve is shown which was obtained for a dimerization model with ϵ_D 2.96 × 10^5 M^{-1} cm^{-1} and $K = 1.69 \times 10^5$ M^{-1}.

Table I. Influence of Electrolytes and Acetone on Absorbance of NiTCPP and CuTCPP Solutions

(a) Experiments with Different Electrolytes

	NiTCPP		CuTCPP	
Electrolyte	λ_{max}, nm	Abs	λ_{max}, nm	Abs
None	411	1.12	413	0.70
KNO_3	408	0.81		
NaCl	407	0.83	406	0.46
$NaNO_3$	407	0.81	406	0.46
LiCl	407	0.83	406	0.46
KCl			406	0.46

(b) Experiments with Acetone and Added Electrolyte

	NiTCPP		CuTCPP	
% acetone	λ_{max}, nm	Abs	λ_{max}, nm	Abs
0	408	0.81	406	0.46
10	413	1.06	413	0.67
20	413	1.12		
30	414	1.12	414	0.85
0[a]	411	1.12	413	0.70
30[a]			414	0.85

[a] No electrolyte.

reasoned that at a given electrolyte concentration, if the deviations from Beer's law were due to electrolyte bonding to the porphyrin, decreasing the dielectric constant of the solvent system should increase this effect. On the other hand, it is known that the addition of organic solvents to aqueous solutions of dimerized porphyrins shifts the equilibrium toward the monomeric form.[14] As may be seen from part b of Table I, acetone tends to undo the electrolyte effect.

Plots of absorbance *vs.* wavelength at a fixed value of path length times metalloporphyrin concentration result in isosbestic points for NiTCPP (Figure 4) and CuTCPP (Figure 5). Therefore, we conclude that within the concentration range of these studies, only one aggregate, the dimer, is formed. The absorbance data were analyzed in terms of a dimerization model

$$2\mathrm{MTCPP} \rightleftarrows (\mathrm{MTCPP})_2$$

which leads to an equation published earlier[4]

$$A_\mathrm{M} - A = ((2\epsilon_\mathrm{M} - \epsilon_\mathrm{D})(4KC_0 + 1 - \sqrt{1 + 8KC_0}))/8K$$

where C_0 is the total concentration of MTCPP units; $A_\mathrm{M} = \epsilon_\mathrm{M} C_0$, the absorption the solution would have at this wavelength in the absence of aggregation; A is the measured absorbance of the solution at this wavelength; ϵ_M and ϵ_D are the molar absorptivities of the monomer and dimer, respectively; and K is the concentration equilibrium constant for dimerization at 25° and $\mu = 0.1\ M$ ($K = [(\mathrm{MTCPP})_2]/[\mathrm{MTCPP}]^2$). From the spectral results at low porphyrin concentration and from our studies in the absence of electrolyte, ϵ_M is $2.28 \times 10^5\ M^{-1}\ \mathrm{cm}^{-1}$ for NiTCPP at 411 mμ and ϵ_M is $3.46 \times 10^5\ M^{-1}\ \mathrm{cm}^{-1}$ for CuTCPP at 415 mμ. These lines are shown in Figures 2 and 3 to point out more clearly the influence of aggregation. By using a curve-fitting program we obtain for NiTCPP, ϵ_D $2.70 \times 10^5\ M^{-1}\ \mathrm{cm}^{-1}$ and $K = 1.57 \times 10^5\ M^{-1}$; for CuTCPP, ϵ_D $2.96 \times 10^5\ M^{-1}\ \mathrm{cm}^{-1}$ and $K = 1.69 \times 10^5\ M^{-1}$. In Figures 2 and 3, the data are shown as points and the theoretical curves obtained from the above parameters are also drawn.

Temperature-jump experiments were conducted for both metalloporphyrins and the data were analyzed in terms of the equation[4]

$$\tau^{-2} = \frac{8k_{22}^{\ 2}}{K} C_0 + \frac{k_{22}^{\ 2}}{K^2}$$

where k_{22} is the forward rate constant for dimerization under these conditions and C_0 and K have the same meaning as above. Figures 6 and 7 show plots of τ^{-2} *vs.* C_0 for NiTCPP and CuTCPP, respectively. The linear relation between the reciprocal of the square of the relaxation time and the total concentration of porphyrin units is observed providing a kinetic justification for the dimerization model. The value of the intercept in such an analysis is generally quite inaccurate[15,16] and so we obtain values for k_{22} from the slopes of these lines and the spectrally determined equilibrium constants. We obtain $k_{22} = 6.2 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ and k_{-22} ($=k_{22}/K$) $= 4.0 \times 10^2\ \mathrm{sec}^{-1}$ for NiTCPP and $k_{22} = 4.5 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_{-22} = 2.7 \times 10^2\ \mathrm{sec}^{-1}$ for CuTCPP.

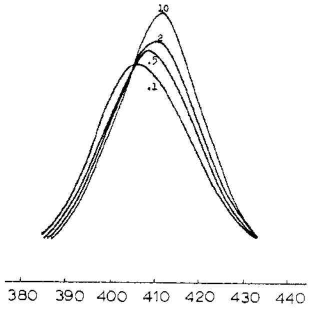

Figure 4. Plot of absorbance *vs.* wavelength for NiTCPP at a fixed value of (cell path length) × (porphyrin concentration). The path lengths are as marked in centimeters.

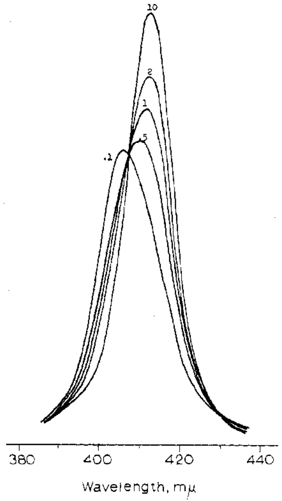

Figure 5. Plot of absorbance *vs.* wavelength for CuTCPP at a fixed value of (cell path length) × (porphyrin concentration). The path lengths are as marked in centimeters.

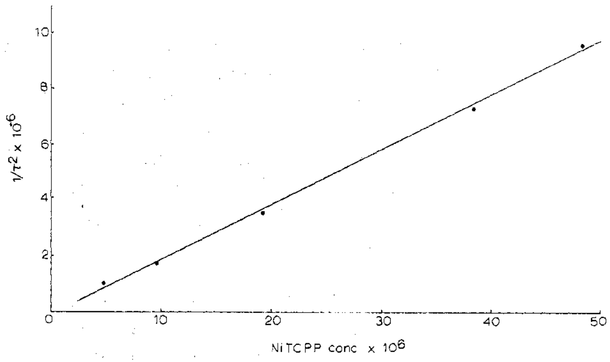

Figure 6. Plot of $1/\tau^2$ *vs.* total concentration of NiTCPP, pH 7.5, $0.1\ M\ \mathrm{KNO_3}$.

Beer's law experiments were conducted in aqueous solution at 0.1 M ionic strength for ZnTCPP. As may be seen from Figure 8, there is no deviation from Beer's law for this porphyrin in the concentration range $10^{-7} <$ [ZnTCPP] $< 5 \times 10^{-5}\ M$. From this experiment we determine ϵ $3.76 \times 10^5\ M^{-1}\ \mathrm{cm}^{-1}$ at 423 mμ. As corroboration for the spectral results, we carried out relaxation experiments and observed no relaxation effects. We also considered the spectra of solutions prepared as above so that the path length times metalloporphyrin concentration is constant. Unlike the results for CuTCPP and NiTCPP, for ZnTCPP over a range of path length from 0.1 to 10 cm all the spectra are superimposable. We conclude, therefore, that while both NiTCPP and CuTCPP are extensively dimerized in aqueous solution at 0.1 M ionic strength, ZnTCPP exists as a monomer under these conditions.

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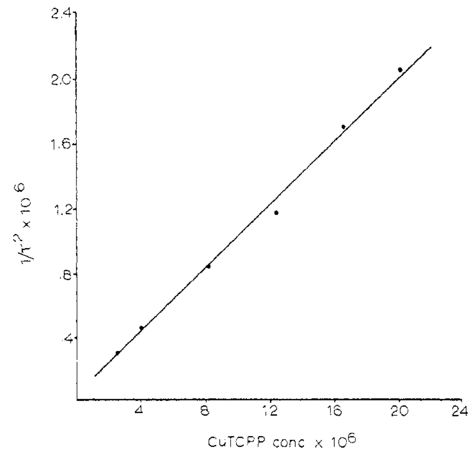

Figure 7. Plot of $1/\tau^2$ *vs.* total concentration of CuTCPP, pH 6.8, 0.1 *M* KCl.

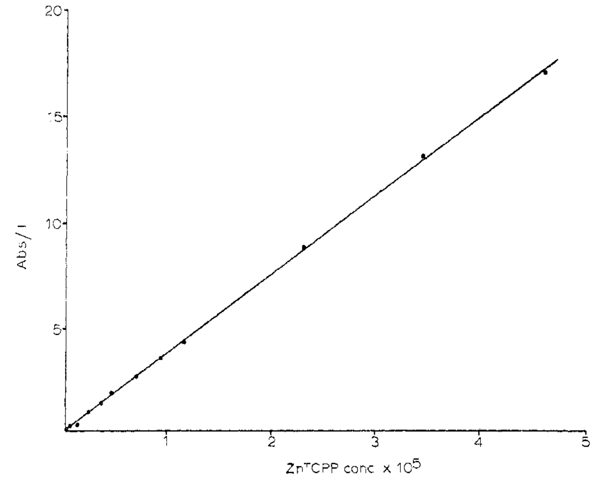

Figure 8. Beer's law experiment for ZnTCPP in water at pH 6.8, 0.1 *M* KNO_3 at 423 mμ.

Discussion

As has been found for the metal-free porphyrins,[4,5] metallo derivatives of TCPP have greater tendency to aggregate than those of TMPyP. Whereas none of the porphyrins, NiTMPyP, CuTMPyP, or ZnTMPyP, shows any tendency to aggregate under the conditions of these experiments, both NiTCPP and CuTCPP dimerize although ZnTCPP does not. We have found that added electrolyte promotes the aggregation of NiTCPP and CuTCPP, and, for 1:1 electrolytes, the effect is a general one.

The difference in tendency to dimerize for metal-free, water-soluble meso-substituted porphyrins has been correlated with the charge type at the periphery of the molecule. It has been suggested that positive charges at the periphery cause the π-electron cloud of porphyrin ring systems to be more diffuse over the surface of the molecule while the negative charges at the periphery tend to localize the electron density near the center, leading to stronger van der Waals interactions for a stacking-type dimer.[4,5] Close approach of the porphyrin monomers is inhibited due to coulombic repulsions and little evidence for aggregation is found for TCPP or its metal derivatives in the absence of electrolyte. The added electrolyte likely creates an ionic atmosphere of opposite charge about the porphyrin unit which leads to a lowering of the coulombic barrier to close approach of the ions.

Our aggregation studies on TCPP and its derivatives lead to an ordering of decreasing stability of dimers of CuTCPP ≈ NiTCPP ≳ TCPP >>> ZnTCPP. The stability constants for CuTCPP, NiTCPP, and the TCPP free base porphyrin agree to within a factor of 4 (see Table II). For there to be no experimental evidence for aggregation of ZnTCPP under the conditions of these experiments implies that the stability constant for dimerization for this porphyrin must be less than 100 M^{-1}. Therefore, the dimer stability constants for CuTCPP, NiTCPP, and TCPP are at least 3 orders of magnitude greater than that for ZnTCPP. Aggregation studies in aqueous solution have been carried out with 4,4′,4″,4‴-tetrasulfophthalocyanine (TSP) and this substance dimerizes much more extensively than does TCPP.[17,18] From the stability data given,[18] the dimerization constant for TSP at 0.1 *M* ionic strength and 25° can be estimated at greater than 10^8 M^{-1} as compared to 4.6×10^4 M^{-1} for TCPP. A number of metal derivatives of TSP have been shown to dimerize with the stability of the dimers decreasing in the order CuTSP ≳ TSP > Fe^{III}TSP > (V^{III}O)TSP ~ ZnTSP > Co^{II}TSP, the stability constant for the formation of the copper dimer being about comparable to the metal-free compound and about 1 order of magnitude greater than for the zinc dimer.[17-20] Therefore, although differences in magnitude exist between dimerization of TCPP and its derivatives with that of TSP and its derivatives, the general trends of stabilities seem to parallel one another for both classes of substances.

Table II. Stability and Rate Constants for Dimerization of Porphyrins and Related Materials ($\mu = 0.1$ *M*; 25°)

	K, M^{-1}	k_f, M^{-1} sec^{-1}	k_r, sec^{-1}
TEP IX[a]	4.3×10^6	2×10^8	50
$TPPS_3$[b]	4.82×10^4	2.2×10^8	4.6×10^3
TCPP[b]	4.55×10^4	6.4×10^7	1.4×10^3
CuTCPP	1.69×10^5	4.5×10^7	2.7×10^2
NiTCPP	1.57×10^5	6.2×10^7	4.0×10^2
$ZnOEP^+$[c]	2.6×10^4	1.3×10^8	5.0×10^3
VOTSPC[d]	5×10^6	4.5×10^6	0.9

[a] References 5 and 14. [b] Reference 4. [c] Reference 15. In $CHCl_3$-MeOH; 20°. [d] R. D. Farina, D. J. Halko, and J. H. Swinehart, *J. Phys. Chem.*, 76, 2343 (1972). $\mu = 0.006$; 28°.

For the copper derivatives, the coordination number at the metal center is most certainly 4[21] while for ZnTCPP, the zinc atom is probably about 0.3 Å out of the porphyrin plane and the coordination number is 5 with a water molecule occupying an axial position.[22] Some ambiguity exists as to the coordination number of the metal center in NiTCPP, although the presence of only one Soret band implies that only one coordination environment is important for this porphyrin. Unfortunately, NiTCPP is not sufficiently soluble in water for us to determine the magnetic moment in solution using the Evans method.[23] We made use of this method to interpret the complex Soret spectrum of NiTMPyP and the influence of acetone.[13] However, compared to NiTMPyP solution spectra, the addition of acetone to NiTCPP has little influence on the spectrum and the influence it does have may be interpreted as arising from the destabilization of the porphyrin dimer (Table I). We conclude, there-

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fore, that the metal center in NiTCPP is not bonded to axial ligands in aqueous solution. This conclusion is consistent with the observation that as the basicity of porphyrin nitrogen atoms increases, the donation of electron density to the nickel atom increases and that this is reflected in a decreased tendency for the nickel atom to bind axial ligands.[24,25] TCPP is considerably more basic than TMPyP and therefore NiTCPP should have less tendency to add water molecules in the axial positions than does NiTMPyP. Therefore, we conclude that the two metallo derivatives of TCPP which dimerize have the metal in the plane and no bonds to axial ligands whereas ZnTCPP has the metal out of the porphyrin plane and bonded to an axial water molecule. These two conditions, that the metal ion is out of the plane with the resulting influence on the π-electron density and that axial ligands are present to interfere with the close approach of the porphyrin planes, lead, we suggest, to ZnTCPP remaining monomeric in solution.

A summary of thermodynamic and kinetic results of a number of porphyrins is shown in Table II. There is very little variation in the forward rate constants for the porphyrin materials (5×10^7-$2 \times 10^8 M^{-1}$ sec^{-1}) although there is considerable variation in solvent system and nature of the porphyrin material (substitution at meso positions and at pyrrole rings). The dimerization rate constant for ($V^{II}O$)-TSP has been studied at $\mu = 0.006 M$[19] and it has been shown that association rate constants for phthalocyanines increase with increasing ionic strength.[20] The activation energy for dimerization of (VO)TSP is 4.9 kcal/mol as compared to 4.1 kcal/mol obtained for TEP IX.[14] Therefore, we conclude that the dimerization of (VO)TSP as well as that for the porphyrin materials is a nearly diffusion-controlled process. That the rate constants are somewhat less than limiting values may reflect solvent structural rearrangement, electrostatic repulsion, and geometric requirements for effective collisions. It is believed that these dimers are of a stacking type[4,15] and the porphyrin ring systems must encounter one another in a proper orientation for dimer formation. This should be reflected in unfavorable entropies of activation and these have been observed.[14,15,19]

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Registry No. NiTMPyP, 41699-90-5; CuTMPyP, 41667-72-5; ZnTMPyP, 41699-91-6; NiTCPP, 41699-92-7; CuTCPP, 41699-93-8; ZnTCPP, 26747-84-3.

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Mass Spectrometry and Structures of Copper(I) Carboxylates in the Vapor Phase

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The copper(I) complexes of the saturated monocarboxylic, acetic, trimethylacetic, and trifluoroacetic acids as well as the complexes of the unsaturated monocarboxylic, acrylic, vinylacetic, and benzoic acids have been synthesized. Vapor pressure measurements, mass spectra, and vapor-phase infrared spectra have shown that all the copper(I) carboxylates are dimeric in the vapor phase. The ease of sublimation of these carboxylates suggests that there is a similarity between the structures of these complexes in the vapor phase and in the solid state. The presence of dimeric units in the crystal structure of copper(I) acetate lends additional support to this hypothesis.

Introduction

The simple aliphatic monocarboxylic acids such as formic acid and acetic acid react with numerous metal ions to form metal carboxylates. One of the most interesting metal carboxylates is copper(II) acetate. Its dimeric structure[1] and its novel magnetic properties[2] have provided a fresh impetus to the investigation of metal carboxylates. The corresponding copper(I) carboxylates however seem to have attracted little attention probably because they are difficult to obtain free of copper(II) contamination and because they are extremely sensitive to oxygen and water. Despite these difficulties, we have initiated a systematic study of the copper(I) carboxylates as a result of our observation that they have a relatively high vapor pressure and are stable in the vapor phase at temperatures up to about 100°.

The syntheses of several copper(I) carboxylates have been reported many years ago: copper(I) formate was prepared by the dissolution of copper(I) oxide in formic acid;[3] copper(I) acetate was obtained in low yields by the thermal decomposition of copper(II) acetate *in vacuo*[4] or by the reduction of copper(II) acetate with hydroxylamine;[5] copper(I) benzoate was isolated as an intermediate in the reduction of copper(II) benzoate with hot benzaldehyde,[6] and copper(I) trifluoroacetate was obtained in the course of the synthesis of the carbonyl complexes.[7] With the exception

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