of conjugated imine double bonds. Unlike sodium borohydride, it will not effect the hydrogenation of isolated imine functions. To further demonstrate this selectivity, hypophosphorous acid was added to solutions of the cobalt(III) complexes of Me$_4$[14]1,8-dieneN$_4$ (III), Me$_4$[14]1-eneN$_4$ (IV), Me$_6$[14]-1,4,8,11-tetraeneN$_4$ (V),[4,25] Me$_6$[14]4,11-dieneN$_4$ (VIII),[26] and Me$_6$[14]4,14-dieneN$_4$ (IX)[27] all of which contain only isolated imine functions. No reaction was observed at room temperature. Upon gently warming, these green solutions become pale brown and within 1 h, a pale pink product precipitates. Aeration and acidification of the filtrate produce, in each case, the starting material ($\leq$50% yield) as verified by the infrared and NMR spectra. The pink product has been identified as anhydrous Co(H$_2$PO$_2$)$_2$. The analytical figures 28.88% C, 2.26% H, and 32.76% P are in agreement with this formulation. The solid decomposes at 270 °C and dissolves in water to give $[\mathrm{Co(H_2O)_6}]^{2+}$, as identified by the visible spectrum,[28] 19 600 (sh) and 21 600 cm$^{-1}$. The infrared spectrum of the pink solid shows three sharp bands in the 2390–2440-cm$^{-1}$ region, four sharp bands in the 1060–1170-cm$^{-1}$ region, two strong bands near 8.5 cm$^{-1}$, and a band at 510 cm$^{-1}$, all attributable to $\mathrm{H_2PO_2}^-$.[29] Thus, hypophosphorous acid will reduce only conjugated imines or the central metal ion in the case of cobalt complexes.

The visible spectrum of [Co(Me$_4$[14]1,8-dieneN$_4$)Cl$_2$]ClO$_4$ shows two low-intensity bands ($\epsilon \sim 50$) at 16 300 and 22 200 cm$^{-1}$ with an intense charge-transfer band at 37 700 cm$^{-1}$ ($\epsilon \sim 10\,000$). Analysis of the spectrum after the method of Wentworth and Piper[30] leads to the values $Dt = 674$, $Dq^z =$ 1420, and $Dq^{xy} = 2600$ cm$^{-1}$. The precursor complex [Co(Me$_4$[14]1,3,8,10-tetraeneN$_4$)Cl$_2$]ClO$_4$ has a ligand field strength $Dq^{xy}$ of 2780 cm$^{-1}$.[17] The complexes [Co(Me$_4$-[14]1,8-dieneN$_4$)Br$_2$]ClO$_4$ and [Co(Me$_2$[14]1-eneN$_4$)Br$_2$]-ClO$_4$ both show a single d–d transition at 15 400 and 15 200 cm$^{-1}$, respectively. The ligand field strength of the macrocyclic ligand Me$_2$[14]1-eneN$_4$ has been estimated, assuming $Dq^z$(Br) = 1277 cm$^{-1}$,[17] to have a value of 2520 cm$^{-1}$. By comparison, the ligand field strength of Me$_4$[14]1,3-dieneN$_4$, based on the dibromo complex, has been calculated to be 2630 cm$^{-1}$.[1]

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**Registry No.** [Co(Me$_4$[14]1,3,8,10-tetraeneN$_4$)Br$_2$]Br, 39177-15-6; [Co(Me$_4$[14]1,8-dieneN$_4$)Br$_2$]ClO$_4$, 61491-31-4; [Co(Me$_4$[14]1,8-dieneN$_4$)Cl$_2$]ClO$_4$, 61491-33-6; [Co(Me$_2$[14]1-eneN$_4$)Br$_2$]ClO$_4$, 61491-35-8; [Co(Me$_2$[14]1,3-dieneN$_4$)Br$_2$]ClO$_4$, 39483-62-0.

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## Kinetics of Copper Incorporation into Tetra(2-*N*-methylpyridyl)porphine. Effects of Basicity on Rate

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This note is concerned with the question of how the rate of metal ion incorporation into porphyrins to form metalloporphyrins is influenced by the basicity of the porphyrin molecule. In aqueous detergent solutions used to solubilize substituted deuterioporphyrin esters, the rates of copper incorporation paralleled porphyrin basicity.[1] However, in pyridine–water media,[2] other workers found that the rates of zinc porphyrin formation were independent of porphyrin basicity. Although plots of $\Delta G^{\ddagger}$ vs. Hammett $\sigma$ values were presented[3,4] for copper metallation reactions in DMF, the reactions were run near the isokinetic temperature, and the observed rates were similar in magnitude. Related behavior was found for copper ligation of a series of natural porphyrin types studied in unbuffered ethanol solutions.[5]

We report a study of copper incorporation in aqueous solution into tetra(2-*N*-methylpyridyl)porphine, TMPyP(2). In contrast to other porphyrins,[6] this ortho isomer remains in the free base (H$_2$P) form in acidic solution. The rate law and activation parameters are compared with the more basic 3- and 4-*N*-methyl isomers,[7,8] TMPyP(3) and TMPyP(4).

### Experimental Section

The tetramethylated porphyrin isomers were prepared by literature methods.[6] It is noted that microcrystalline metal derivatives of TMPyP(2) can be obtained by adding a concentrated solution of sodium perchlorate to a cooled solution of the metalloporphyrin nitrate, and refrigerating overnight. Since several of our perchlorate samples have exploded while drying, and other workers have noted similar behavior,[9] *the preparation of anhydrous perchlorates in the TMPyP series should be attempted with extreme caution.*

Cu–TMPyP(2) was made in solution by addition of an excess of copper nitrate to H$_2$–TMPyP(2) at pH 1. The absorption spectra as a function of time showed excellent isosbestic points at 675, 587, 525, and 478 nm, with major bands at 415 nm ($\epsilon$ 1.34 × 10$^5$), 543 nm (1.88 × 10$^4$) and 578 nm (1.17 × 10$^4$). The latter band appears as a shoulder in the 3- and 4- copper isomers. The copper adducts did not solvolyze after sitting for days at room temperature in 1.0

**Table I.** Rate Data for the $Cu^{2+}/H_2$-TMPyP(2) Reactions at 61.7 °C

| pH | $10^3(Cu^{2+})_0$, M | $(NO_3^-)_0$,$^a$ M | $10^2k_0$, $min^{-1}$ | $k_0/(Cu^{2+})_0$-$(NO_3^-)_0$, $M^{-2}$ $min^{-1}$ |
|---|---|---|---|---|
| 0.97 | 32.0 | 1.74 | 37.4 | 6.7 |
| 0.97 | 24.0 | 1.76 | 26.7 | 6.3 |
| 0.98 | 16.0 | 1.77 | 17.3 | 6.1 |
| 0.99 | 8.0 | 1.79 | 10.3 | 7.2 |
| 1.00 | 4.0 | 1.79 | 4.80 | 6.7 |
| 1.00 | 4.0 | 1.59 | 4.45 | 6.9 |
| 1.00 | 4.0 | 0.99 | 2.60 | 6.5 |
| 1.00 | 4.0 | 0.79 | 1.98 | 6.2 |
| 1.00 | 4.0 | 0.59 | 1.41 | 6.0 |
| 2.40 | 16.0 | 1.77 | 16.9 | 6.0 |
| 1.85 | 16.0 | 1.77 | 21.2 | 7.5 |
| 1.27 | 16.0 | 1.77 | 21.2 | 7.5 |
| 0.69 | 16.0 | 1.77 | 18.0 | 6.3 |
| 0.39 | 16.0 | 1.77 | 16.2 | 5.7 |
| | | | | Av 6.6 ± 0.5 |

$^a$ $\mu = 2.0$ ($LiNO_3/HNO_3$) for all $(NO_3^-)_0 = 1.7$ runs.

**Table II.** Activation Parameters for the $Cu^{2+}/H_2$-TMPyP(*x*) Reactions (Comparisons with Acid Solvolysis Rates)

| | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, eu | $k$(39 °C) $Cu/PH_2$, $M^{-2}$ $min^{-1}$ $^a$ | $10^5k$ (25 °C) $ZnP/H^+$,$^b$ $s^{-1}$ $^b$ |
|---|---|---|---|---|
| $H_2$-TMPyP(4) | 10.1 | −22 | 482 | 420 |
| $H_2$-TMPyP(3) | 11.7 | −16 | 742 | 728 |
| $H_2$-TMPyP(2) | 16.0 | −15 | 1.2 | 0.4 |

$^a$ $k = k_0/(Cu^{2+})_0(NO_3^-)_0$. $^b$ Data from ref 6, in 1.0 M $HNO_3$.

M $HNO_3$. All reactions went to completion. The kinetic and equilibrium studies were done by previously described methods.[7,8]

## Results

**Basicity of TMPyP(3).** For the $H_3P^+/H_2P$ equilibira, $pK_3$ was determined to be 1.8 ± 0.1 at 25 °C, $\mu = 0.2$ ($HNO_3/NaNO_3$) for $H_2$–TMPyP(3), as compared[7] with 1.4 ± 0.1 for $H_2$–TMPyP(4), under similar conditions.

**Copper Incorporation into TMPyP(2).** The rate of copper incorporation into $H_2$–TMPyP(2) was studied at 61.7 °C in $LiNO_3/HNO_3$ solutions. Under pseudo-first-order conditions with an excess of total copper over porphyrin, the observed rates were first order in porphyrin over three half-lives. As shown in Table I at $\mu = 2.0$, the rates were independent of pH from pH 0.4 to 2.4, and first order in total copper over an eightfold range. The empirical kinetic data are best described by a first-order term in nitrate. Thus,

$$\text{rate} = k(Cu^{2+})_0(NO_3^-)_0(H_2\text{-TMPyP(2)})$$

with $k = 6.6 \pm 0.5$ $M^{-2}$ $min^{-1}$ at 61.7 °C.

**Activation Parameters.** The activation parameters for copper incorporation into the free base forms of the three porphyrin isomers at pH 3.2 ($HNO_3/LiNO_3$) were determined from kinetic studies in the temperature range of 33–62 °C. The results are listed in Table II. .

## Discussion

TMPyP(2) showed no spectral evidence[6] for protonated $H_3P^+$ or $H_4P^{2+}$ forms from pH 7 to 0, and the rate law for copper incorporation is hydrogen ion independent from pH 3.2 to 0.4. This is in contrast to TMPyP(4) and other porphyrins,[7,8] where the rate of metallation decreases with pH owing to the formation in acid of unreactive protonated species. For example,[7] metal incorporation into TMPyP(4) (which has recently been suggested[10] as a student kinetics project) decreases by a factor of 2500 from pH 3 to 0.

In common with many reactions[11] of TMPyP(4), the formally tetrapositive TMPyP(2) contains an anion term in its rate law. Although the inclusion of this term gives an empirical rate equation in excellent agreement with the ionic strength dependence of the rate, we are yet unable to separate the intrinsic ionic strength dependence of this reaction between two positive ions from a possible genuine anion catalysis in the incorporation process. Steric models indicate hindered rotation of the ortho *N*-methyl groups in TMPyP(2), and thus a statistical distribution of the four conformers should exist. They all appear to be equally reactive, however, since isosbestic points were obtained, and no deviation from first-order kinetics could be detected.

The rate laws for the 2-, 3-, and 4- isomers are the same; first order in copper, free base porphyrin, and nitrate. $H_2$–TMPyP(3) is approximately 2.5 times as basic toward protons as is $H_2$–TMPyP(4), a possible consequence of the lack of direct resonance conjugation of the meta pyridine positions with the porphyrin ring. The basicity of the isomers is thus $3 > 4 \gg 2$, and toward their free base forms the relative rates of copper incorporation at 39 °C are 618:410:1, respectively.

Going from the para to ortho isomers, the *N*-methyl group is moved closer to the reaction center. This change is accompanied by an increase in both the activation enthalpy and entropy, and exactly the same trend is found[3] in the $CuCl_2$/DMF system with *p*-, *m*-, and *o*-methyl substituted tetraphenylporphyrins. $Ni^{II}$–TMPyP(4) in water is at 25 °C approximately a 1:1 equilibrium mixture[9] of diamagnetic square-planar molecules and paramagnetic, axially water-ligated six-coordinate species. $Ni^{II}$–TMPyP(2) is tentatively concluded[12] to be almost exclusively in the six-coordinate state under the same conditions. Thus desolvation of the central porphyrin cavity itself during metal ion incorporation could contribute to the higher activation energy and more favorable entropy found for $H_2$–TMPyP(2) as compared with the 4-isomer.

In conclusion, the rates of copper incorporation into the free base forms of a series of TMPyP isomers increase as the basicity of the porphyrin toward protons increases. As noted in Table II, the observed acid solvolysis rates[6] of the same series of zinc porphyrin isomers also increase in a similar fashion[11] with porphyrin basicity. Such solvolysis–basicity trends have been noted before.[11] Thus formation and dissociation rates are sensitive both to the total porphyrin charge type (positive or negative) and, within a given peripheral charge type, to the position of the charge around the porphyrin periphery. In general, the charge type and positions correlate with the basicity of the porphyrin toward protons.

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**Registry No.** $H_2$–TMPyP(4), 38673-65-3; $H_2$–TMPyP(3), 59728-91-5; $H_2$–TMPyP(2), 59728-89-1; $Cu^{2+}$, 15158-11-9; Cu-TMPyP(2), 61827-28-9.

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