TABLE I
REACTIONS OF 1,4-COD WITH SOME TRANSITION METAL IONS

Reactant	Product	Color	Mp (dec), °C	Ir	Olefin obtained upon decompn[a]
$RhCl_3 \cdot 3H_2O$	$[Rh(1,5\text{-COD})Cl]_2$	Yellow	220		1,5-COD
$IrCl_3 \cdot 3H_2O$	$[Ir(1,5\text{-COD})HCl_2]_2$	Yellow	198	ν_{Ir-H}, 2256	1,5-COD
$Pd(C_6H_5CN)_2Cl_2$	$Pd(1,4\text{-COD})Cl_2$	Yellow	141	$\nu_{C=C}$, 1510	1,4-COD
K_2PtCl_4	$Pt(1,5\text{-COD})Cl_2$	White	138–139		1,5-COD
CuCl	$[Cu(1,4\text{-COD})Cl]_2$	White	113–114	$\nu_{C=C}$, 1615, 1495 ν_{Cu-Cl} (bridging), 348, 320	1,4-COD
$AgNO_3$	$[Ag(1,4\text{-COD})Ag](NO_3)_2$	White	110–111	$\nu_{C=C}$, 1600	1,4-COD
$HAuCl_4$	Unstable	White			1,4-COD

[a] Decomposition was accomplished by treating the complex with aqueous KCN and extracting the olefin with ether. The $AgNO_3$ complex was decomposed with aqueous NH_3 solution.

by the reaction of 0.50 g of $HAuCl_4$ in 20 ml of H_2O with 1 ml of 1,4-COD.

Results and Discussion

1,4-COD can be conveniently prepared by optimizing the conditions of the homogeneous catalytic isomerization of 1,5-COD to 1,3-COD to give a maximum yield of the intermediate 1,4-COD. The number of moles of 1,5-COD used per mole of the catalyst is 1000. The catalyst can be recovered and reused frequently with no decrease in its catalytic activity. However, small amounts of $SnCl_2 \cdot 2H_2O$ must be added every time a second-hand catalyst is used.

1,4-COD reacts readily with transition metals with almost-filled d orbitals in their low oxidation states. This reflects the importance of π bonding involving electron back-donation in the olefin–metal complexes. The behavior of Ir(III) which, unlike Rh(III), retains its high oxidation state may suggest that π bonding in Ir, and probably in other heavier atoms, is less important than σ bonding.

Ions which are known to react with 1,3-COD react readily with 1,4-COD. Thus Ag(I) which gives a complex with 1,5-COD stable in solution up to 75° and a complex with 1,3-COD stable in solution only below 0° gave a 1,4-COD–Ag^I complex stable at 40° in solution. The behavior of 1,4-COD with Pd(II) *vs.* that of 1,3-COD and 1,5-COD parallels its behavior with Ag(I). Moreover, some ions, *e.g.*, Cu(I), which do not react with 1,3-COD but give stable complexes with 1,5-COD, did give rather unstable complexes with 1,4-COD. This intermediate behavior of 1,4-COD may be attributed to the position of the two double bonds in the olefin. They are far enough from each other to give complexes more stable than those of 1,3-COD and too close to give complexes as stable as those of 1,5-COD.

Closer examination of the behavior of Ag(I) shows this steric effect very clearly. 1,5-COD may span the two coordination sites on opposite sides of the Ag^+ ion, though not necessarily at exactly 180°, thus forming $[Ag(1,5\text{-COD})]^+NO_3^-$. 1,4-COD, on the other hand, acts as a bridge between two Ag^+ ions giving $[Ag(1,4\text{-COD})Ag]^{2+}(NO_3)_2{}^{2-}$.

The ir spectrum of the 1,4-COD–Cu^I complex shows two absorptions assigned to C=C at 1615 and 1495 cm^{-1}. This suggests that one double bond is much closer to the metal atom than the other. It also reflects the weaker bonding in $[Cu(1,4\text{-COD})Cl]_2$ compared to that in $[Cu(1,5\text{-COD})Cl]_2$ in which $\nu_{C=C}$ is reduced by about 165 cm^{-1} from its free-olefin value.

The transition metal ions investigated in this work can be classified into three categories with respect to their reaction with 1,4-COD. (1) Ions which give 1,4-COD–metal complexes. The olefin does not rearrange in these complexes. These ions include Ag(I), Cu(I), and Au(III). (2) Ions which give 1,5-COD–metal complexes. 1,4-COD rearranges in complexes of these ions to the better chelating 1,5-COD. Such ions include Pt(II), Rh(III), and Ir(III). These same ions are known to yield 1,5-COD–metal complexes in their reaction with 1,3-COD. The rearrangement of 1,3-COD to 1,5-COD in these complexes probably proceeds *via* the intermediate formation of 1,4-COD which rearranges in a very fast step to the 1,5 isomer.[6] This explains the failure to detect 1,4-COD as reaction intermediate in the 1,3 to 1,5 rearrangement by these ions. (3) Ions which may give 1,4-COD–metal complex or rearranged 1,5-COD–metal complex depending on the reaction conditions. Pd(II) stands unique in this category. The reason for the different behaviors of various ions may be related to the size of the ion involved.

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Kinetic Differences between the Incorporation of Zinc(II) and Cadmium(II) into Porphyrins and *N*-Methylporphyrins[1]

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While a number of studies have appeared concerning the mechanisms of incorporation of divalent metal ions into porphyrin molecules to form metalloporphyrins,[2-13]

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little work has been done on the formation kinetics of metal complexes of *N*-alkylporphyrins, in which an alkyl group is substituted for a proton on the central nitrogen atoms of a porphyrin. *N*-Methyl- and -ethyl-,[14,15] *N,N'*-dimethyl-,[16,17] and *N,N',N''*-trimethylporphyrin[18] are known. Zinc– and copper–chloro complexes of *N*-methylporphyrins have been prepared, and a zinc ion catalyzed demethylation of an *N*-methylporphyrin has been observed.[19] The kinetics of the acid-catalyzed solvolysis of a zinc *N*-methylporphyrin has also been described.[20]

We report the kinetic differences between zinc and cadmium ion incorporation into etioporphyrin(III) and *N*-methyletioporphyrin(III) in dimethylformamide

$$\mathrm{M(II)} + \mathrm{PH_2} \longrightarrow \mathrm{PM} + 2\mathrm{H^+} \tag{1}$$

$$\mathrm{M(II)} + \mathrm{CH_3PH} \longrightarrow \mathrm{CH_3PM^+} + \mathrm{H^+} \tag{2}$$

Experimental Section

Dimethylformamide (DMF) was dried by refluxing over BaO and distilled. Etioporphyrin(III) (Etio)[21] and *N*-methyletioporphyrin(III) (*N*-MeEtio)[14] were prepared by literature methods. Their zinc and cadmium complexes were made by briefly refluxing the porphyrins with metal chloride salts in DMF[22] until the typical four-banded free-base porphyrin spectra disappeared. The absorption spectra of the metal complexes were similar to those of other metalloporphyrins,[23] and the band positions (in nm) and ratios of bands I and II in DMF are as follows: ZnEtio, 575, 539, 408 (1.03); CdEtio, 582, 547, 416 (0.637); Zn-*N*-MeEtio, 582, 535, 417 (1.63); Cd-*N*-MeEtio, 587, 542, 427 (1.53). The complexes could be hydrolyzed with dilute HCl, and the acid spectra produced were characteristic of Etio and *N*-MeEtio, showing that demethylation did not occur under the reaction conditions.

The kinetics were followed by observing the decrease with time of band IV of the free base porphyrins, at 497 nm for Etio on a Cary 14 recording spectrophotometer and at 505 nm for *N*-MeEtio using a Durrum stopped-flow apparatus. The absorption bands of the metal complexes were of negligible intensity at these wavelengths. The reactions were run under pseudo-first-order conditions with the initial metal chloride concentration at least 30-fold greater than the porphyrin (*ca.* 1×10^{-5} *F*) concentration. Plots of log $(D_x - D_\infty)$ *vs.* time were linear over 2 half-lives showing the reaction to be first order in free-base porphyrin. (D_x is the absorbance at a given time while D_∞ is the absorbance after 7 half-lives.) The slopes of such plots multiplied by 2.303 gave the observed rate constant k_{obsd}, which was independent of initial porphyrin concentration in the range (0.5–2.5) $\times 10^{-5}$ *F*.

Results and Discussion

Tables I and II show that the ratio $k_{\mathrm{obsd}}/[\mathrm{M(II)}]$ is constant at a given temperature for both Cd(II) and Zn(II) with Etio and *N*-MeEtio. The observed rate law is thus

$$\text{rate} = k[\text{metal}][\text{porphyrin}] \tag{3}$$

The activation parameters E and $\Delta S^{\ddagger}$ were calculated[24] from the temperature dependence of the rates and are listed in Table III.

TABLE I

KINETIC RESULTS FOR Zn(II) WITH *N*-MeEtio AND Etio IN DMF

k_{obsd}, $\mathrm{sec^{-1}}$	[Zn(II)], *F*	$k_{\mathrm{obsd}}/[\mathrm{Zn(II)}]$, $F^{-1}\ \mathrm{sec^{-1}}$	Temp, °C
	N-Methyletioporphyrin[a]		
10.2	20.0×10^{-3}	5.08×10^{-2}	25.0
5.37	9.98×10^{-3}	5.39×10^{-2}	25.0
2.63	4.99×10^{-3}	5.27×10^{-2}	25.0
1.24	2.49×10^{-3}	4.97×10^{-2}	25.0
	Av	$(5.2 \pm 0.2) \times 10^{-2}$	
3.69	10.6×10^{-3}	3.48×10^{-2}	16.3
4.48	10.6×10^{-3}	4.23×10^{-2}	20.3
5.45	10.6×10^{-3}	5.12×10^{-2}	25.5
6.75	10.6×10^{-3}	6.37×10^{-2}	29.9
	Etioporphyrin[b]		
7.62×10^{-5}	1.61×10^{-2}	4.74×10^{-3}	21.3
9.49×10^{-5}	2.01×10^{-2}	4.72×10^{-3}	21.3
10.7×10^{-5}	2.41×10^{-2}	4.44×10^{-3}	21.3
16.1×10^{-5}	3.22×10^{-2}	5.00×10^{-3}	21.3
18.9×10^{-5}	4.16×10^{-2}	4.52×10^{-3}	21.3
30.5×10^{-5}	6.28×10^{-2}	4.85×10^{-3}	21.3
	Av	$(4.7 \times 0.3) \times 10^{-3}$	
21.9×10^{-5}	3.22×10^{-2}	6.80×10^{-3}	25.2
80.6×10^{-5}	3.22×10^{-2}	25.1×10^{-3}	45.2
116.8×10^{-5}	3.22×10^{-2}	36.2×10^{-3}	50.8
162.8×10^{-5}	3.22×10^{-2}	50.5×10^{-3}	55.7

[a] [*N*-MeEtio] = 9.2×10^{-6} *F*. [b] [Etio] = 1.2×10^{-5} *F*.

TABLE II

KINETIC RESULTS FOR Cd(II) WITH *N*-MeEtio AND Etio IN DMF

k_{obsd}, $\mathrm{sec^{-1}}$	[Cd(II)], *F*	$k_{\mathrm{obsd}}/[\mathrm{Cd(II)}]$, $F^{-1}\ \mathrm{sec^{-1}}$	Temp, °C
	N-Methyletioporphyrin[a]		
41.0×10^{-1}	35.7×10^{-4}	11.5×10^{2}	25.0
38.0×10^{-1}	31.8×10^{-4}	12.0×10^{2}	25.0
19.3×10^{-1}	15.9×10^{-4}	12.1×10^{2}	25.0
18.9×10^{-1}	15.8×10^{-4}	12.0×10^{2}	25.0
9.49×10^{-1}	8.93×10^{-4}	10.6×10^{2}	25.0
6.97×10^{-1}	6.28×10^{-4}	11.1×10^{2}	25.0
	Av	$(11.5 \pm 0.5) \times 10^{2}$	
17.7×10^{-1}	28.4×10^{-4}	6.24×10^{2}	16.8
22.9×10^{-1}	28.4×10^{-4}	8.07×10^{2}	20.3
33.6×10^{-1}	28.4×10^{-4}	11.8×10^{2}	25.5
43.5×10^{-1}	28.4×10^{-4}	15.3×10^{2}	30.3
	Etioporphyrin[b]		
5.48×10^{-5}	3.17×10^{-3}	17.3×10^{-3}	25.0
6.63×10^{-5}	3.81×10^{-3}	17.4×10^{-3}	25.0
7.21×10^{-5}	4.45×10^{-3}	16.0×10^{-3}	25.0
9.31×10^{-5}	5.08×10^{-3}	18.4×10^{-3}	25.0
14.8×10^{-5}	8.23×10^{-3}	17.9×10^{-3}	25.0
	Av	$(17.4 \pm 0.8) \times 10^{-3}$	
11.4×10^{-5}	5.08×10^{-3}	22.4×10^{-3}	27.0
41.2×10^{-5}	5.08×10^{-3}	81.2×10^{-3}	45.0
82.1×10^{-5}	5.08×10^{-3}	161.5×10^{-3}	50.8
124.2×10^{-5}	5.08×10^{-3}	245.0×10^{-3}	55.6

[a] [*N*-MeEtio] = 9.2×10^{-6} *F*. [b] [Etio] = 1.2×10^{-5} *F*.

TABLE III

ACTIVATION PARAMETERS

	E, kcal/mol	$\Delta S^{\ddagger}$ (25°), eu
Zn(II) + Etio	13.1 ± 0.5	-27 ± 3
Cd(II) + Etio	17.4 ± 0.7	-13 ± 2
Zn(II) + *N*-MeEtio	8.0 ± 0.3	-21 ± 3
Cd(II) + *N*-MeEtio	12.4 ± 0.6	-5 ± 2

The observed rate law is of the form most commonly observed for the incorporation of metal ions into porphyrins[2–4,6,10–13] and is seen to be applicable to *N*-methylporphyrins also. This observation has im-

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portance in that, while a metal ion can attack a porphyrin molecule from both above and below, the *N*-methyl group completely blocks to metal ion attack one of the axial positions of an *N*-methylporphyrin. Studies with systems in which "sitting-atop" species are formed in aqueous solution[5,7] show rate laws which are second order in metal ions and presumably involve one ion on each side of the porphyrin plane. Therefore in systems showing simple first-order metal ion kinetics, it cannot be ruled out that a second faster metal ion dependent step follows the slower rate-determining step, in a scheme such as

$$\mathrm{M + PH_2 \longrightarrow [MPH_2]} \quad \text{slow} \qquad (4)$$

$$\mathrm{M + [MPH_2] \longrightarrow [MPH_2M] \longrightarrow MP + 2H^+ + M} \quad \text{fast} \qquad (5)$$

Since *N*-MeEtio obeys the same rate law as Etio, the implication is that such a second step does not occur with most porphyrins.

Etio and *N*-MeEtio each incorporate Cd(II) about twice as rapidly as Zn(II) in DMF (Tables I and II). In aqueous solutions[5] and in acetic acid solvents,[4] the reverse situation is found; that is, zinc inserts hundreds of times faster than cadmium ions. Such solvent-dependent rate reversals are also shown by Cu and Zn: in acetic acid[13] Zn > Cu, while in 8.3% acetic acid–water[4] and water[5] Cu > Zn. For both Etio and *N*-MeEtio, although the zinc reactions have lower energies of activation by about 4 kcal than those of cadmium, the cadmium reactions have higher entropies of activation (*ca.* 14 eu) than zinc. The higher charge: radius ratio of zinc compared to cadmium would favor a stronger zinc to porphyrin bond in the activation complex in line with the low zinc activation energy. The same factor would tend to increase solvent orientation in the activated complex more with zinc than with cadmium. Such ordering is expected to be important in the low dielectric solvent DMF.[25] There thus appears to be no *intrinsic* order of metal ion formation rates with porphyrins.

Tables I and II show that metal ion incorporation rates are about 10^5 faster into *N*-MeEtio than Etio. It is known that *N*-methylporphyrins are stronger bases toward protons than are porphyrins.[15,17] This is presumably due to the extremely nonplanar nature of *N*-methyl species, with the bulky methyl group preventing porphyrin planarity and thereby causing the central nitrogen atoms to tilt in a direction away from the porphyrin center and more toward the solvent environment. In terms of the free base–monocation equilibria

$$\mathrm{PH_3^+ = PH_2 + H^+} \qquad \mathrm{p}K_3 \qquad (6)$$

corproporphyrin[26] has pK_3 = 7.16 and *N*-methylcorproporphyrin shows pK_3 = 11.3. The differences in pK should be similar for Etio and *N*-MeEtio. Studies with 2,4-disubstituted deuteroporphyrins[23] show that the rates of Cu(II) incorporation increase with porphyrin basicity. Thus meso-, proto-, and diacetylporphyrins having pK_3 values of 5.8, 4.8, and 3.3, respectively, give relative incorporation rates of 7.0, 2.5, and 1.0. On this basis, the *N*-MeEtio reactions should be no more than 200-fold faster than those of Etio, since Etio has two sides vacant for attack whereas *N*-MeEtio has only one. Thus basicity and statistical factors alone cannot account for the marked rate differences.

One model for metal ion incorporation[27] would involve a transition state with the porphyrin bent such that the two opposite pyrrole lone pairs are coordinated to the metal ion with the other two pyrrole groups bent in the opposite direction to facilitate proton dissociation. The inherent nonplanarity of *N*-MeEtio compared to Etio indicates that less energy would be expended to form such a bent activated complex with the *N*-methyl species, thus favoring a faster metal ion incorporation. Another factor favoring the *N*-MeEtio rate is the amount of partial positive charge formed as a result of the incipient dissociation of two protons in Etio and one in *N*-MeEtio in the transition state. Insofar as this charge will order the surrounding solvent, the entropy increase should be in favor of the *N*-MeEtio system. Similarly the amount of solvent reorganization about the metal ion should be less stringent with *N*-MeEtio than Etio, since a three- rather than four-coordinate (with respect to porphyrin) species is to be formed.

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Miscibility in the Systems Sodium Iodide–Trisodium Bismuthide and Sodium Iodide–Trisodium Antimonide[1]

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An earlier study[3] revealed that the intermetallic phases $\mathrm{Na_3Bi}$ and $\mathrm{Na_3Sb}$ exhibited sizable solubilities in molten sodium halides. For example, the NaI–NaCl eutectic composition was found to dissolve up to 26 mol % $\mathrm{Na_3Bi}$ at 1000° and ~20 mol % $\mathrm{Na_3Sb}$ at 700°. The principal technique employed earlier involved equilibration in sealed tantalum containers followed by rapid quenching and then analysis of the separated salt phase. The question was raised at the time[4] as to whether some segregation and recombination of the once-dissolved intermetallic phase might have taken place even during rapid cooling, thereby giving solubility data lower than equilibrium values. The occurrence of such errors has been well documented in studies of some binary systems in which samples have

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