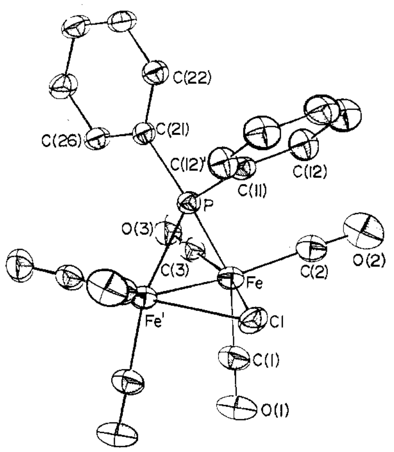

Figure 1. A perspective view of the molecular structure of $Fe_2(CO)_6(Cl)(PPh_2)$. Thermal ellipsoids are drawn at the 30% level, and hydrogen atoms are not shown.

Fe–C(3), 1.772 (4) vs. 1.738 (5) Å). Scattering factor tables, including the anomalous dispersion correction for iron, were taken from ref 3. Scattering factors for hydrogen were those of ref 4. Anistropic thermal parameters are included as supplementary data, Table SI, and a list of observed and calculated structure factors is also available.

Results and Discussion

Figure 1 presents a perspective view of the molecule drawn to illustrate the crystallographic mirror plane passing through the phosphorus atom, the midpoint of the Fe–Fe bond and the bridging chlorine atom. There are no intermolecular contacts of significance. The central Fe_2PCl core, which has a butterfly configuration, provides the main structural features of interest. The Fe–Fe′ bond distance (2.5607 (5) Å) is the shortest and one of the most accurate yet reported for a phosphido-bridged binuclear complex.[5,6] Thus in $Fe_2(CO)_6(PPh_2)_2$ the Fe–Fe bond length is 2.623 (3) Å[5] while in the unsymmetrical derivative $Fe_2(CO)_6(PPhMe)_2$, which has the shortest Fe–Fe bond of any bis(phosphido)-bridged species, the distance is 2.619 (1) Å. Replacement of a bridging diphenylphosphido group by a bridging chloride ligand thus results in a contraction of ~0.06 Å in the Fe–Fe bond length. This result is not inconsistent with the fact that Fe–Fe bond lengths and Fe–P–Fe angles in $Fe_2(CO)_6(X)_2$ complexes show a general decrease along the series X = $PR_2 > SR > NR_2$ as the electronegativity of the bridging atom increases and the covalent radius decreases.[6] The only mixed-bridge complexes for which extensive structural data exist are the zwitterionic hydrocarbyl compounds $Fe_2(CO)_6\{CHC(Ph)NRR'\}(PPh_2)$ (R = c-C_6H_{11}, R′ = H, Fe–Fe = 2.576 (1) Å[7]; R = R′ = Et, Fe–Fe = 2.548 (1) Å[8]), where it is apparent that substitution of PPh_2 in $Fe_2(CO)_6(PPh_2)_2$ by the dipolar carbon ligands $C^-H-C(Ph)N^+RR'$ effects analogous decrements in Fe–Fe distances and Fe–P–Fe angles. The Fe–P–Fe angle of 69.8 (0)° is one of the smallest reported to date for a phosphido bridge. Indeed phosphido bridges are remarkably versatile in that they can support a wide range of bonding and nonbonding metal–metal distances. For phosphido-bridged iron complexes the present Fe–P–Fe angle and Fe–Fe distance are the lower limits with angles ranging up to the value of 98.0 (1)° in $Fe_3(CO)_8[Ph_2PC_4(CF_3)_2]PPh_2$,[9] where the Fe–Fe distance of 4.59 Å is definitely nonbonding. This demonstrable flexibility of PR_2 bridges may be capable of exploitation in the design of binuclear catalysts where a key feature is the generation and cleavage of metal–metal bonds.

Despite the smaller covalent radius of chlorine (0.99 Å) than of phosphorus (1.10 Å) the Fe–Cl bridge bond length 2.289 (1) Å is significantly longer than the Fe–P bond length (2.238 (1) Å). We interpret this as a direct reflection of the poor affinity between an iron carbonyl fragment and the chlorine atom as a ligand. Halogeno carbonyls of iron are few in number and, with the exception of the iodides, unstable and difficult to prepare.[10] It is also notable that the Fe–C(3) distance (trans to Cl) of 1.772 (4) Å is distinctly shorter than the Fe–C bond lengths to carbonyls trans to the Fe–Fe bond (Fe–C(1) of 1.821 (3) Å) or to the Fe–P bond (Fe–C(2) of 1.795 (4) Å) presumably due to the poor trans directing influence of a Cl ligand in this environment.

Finally, we note that the experimental value of the Fe–P–Fe′ angle (69.8 (0)°) is very close to that predicted (~70°) for the halogeno-bridged complexes $Fe_2(CO)_6(X)(PPh_2)$ (X = Br, I) from an analysis of ^{31}P NMR shifts for the phosphorus atom in a variety of phosphido-bridged iron complexes.[1]

Acknowledgment. We are grateful to the National Research Council of Canada for financial support of this work.

Registry No. $Fe_2(CO)_6(Cl)(PPh_2)$, 71000-92-5.

Supplementary Material Available: A listing of structure factor amplitudes and Table SI showing anisotropic thermal parameters (8 pages). Ordering information is given on any current masthead page.

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Activation Parameters and a Mechanism for Metal–Porphyrin Formation Reactions

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The rates of metal ion incorporation into porphyrins to form metalloporphyrins have been shown to vary with the transition-metal type,[1-3] from relatively fast for Cu^{2+} to orders of magnitude slower for Ni^{2+}. Such rates themselves are several million times slower[4] than those of most conventional metal–ligand substitution processes. With the aim of understanding such differences, we have measured the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+} incorporation into tetrakis(*N*-methyl-4-pyridyl)porphyrin in aqueous solution. Similar measurements have been made with porphyrins in acetic acid/water[5] or DMF[6] solutions, where the

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Table I. Activation Parameters for Metal/Tetrakis(*N*-methyl-4-pyridyl)porphyrin Reactions (pH 3.0, $(NO_3^-) = 0.5$ M)

metal	k_I,[a] $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
Cu^{2+}	7.0×10^{-1}	15.4	−7.7
Zn^{2+}	1.6×10^{-2}	15.4	−15.0
Co^{2+}	1.1×10^{-3}	20.4	−3.6
Ni^{2+}	2.1×10^{-6}	12.3	−43.0

[a] At 25 °C.

nature of the metal ion reactant is often in doubt. A mechanism for such metal–porphyrin formation reactions is proposed.

Experimental Section

Tetrakis(*N*-methyl-4-pyridyl)porphyrin (TMpyP(4)) was obtained from Man-Win Coordination Chemicals, Washington, DC, and converted to its perchlorate salt for kinetic measurements by precipitation with sodium perchlorate. The reactions were run under pseudo-first-order conditions with an excess of metal (ca. 5×10^{-2} to 5×10^{-3} M) to total porphyrin (ca. 10^{-5} M). The nitrate concentration was held constant at 0.5 M ($NaNO_3/HNO_3/M(NO_3)_2$) and the pH maintained at 3.0. As before,[7,8] the reactions were found to be first order in metal and porphyrin. The reactions were run from 20 to 40 °C, and the Eyring equation was used to calculate the activation parameters.

Results and Discussion

At constant ionic strength, the overall mechanism for metal ion/TMpyP(4) reactions has been shown to be[8] eq 1–3. The

$$H_4\text{–}P^{2+} = H_3\text{–}P^{+} + H^{+} \quad K_4 \qquad (1)$$

$$H_3\text{–}P^{+} = H_2\text{–}P + H^{+} \quad K_3 \qquad (2)$$

$$H_2\text{–}P + M^{2+} \rightarrow M\text{–}P + 2H^{+} \quad k_I \qquad (3)$$

diacid ($H_4\text{–}P^{2+}$) and monocation ($H_3\text{–}P^{+}$) porphyrin forms are unreactive, and only the free base ($H_2\text{–}P$) incorporates metal ions. The observed rate constant k_o is equal to $k_I(M^{2+})/[1 + (H^+)/K_3 + (H^+)^2/K_3K_4]$. At $I = 0.5$, TMpyP(4) has $pK_3 = 1.7$ and $pK_4 = 0.6$; thus the porphyrin is mainly in the free base form at pH 3. The proton dependence of the reaction arises from the porphyrin–proton preequilibria, as it has been shown that with tetrakis(*N*-methyl-2-pyridyl)porphyrin, TMpyP(2), which is in the free base form[9] at pH values above pH 0, that the metal–porphyrin rate law in the acid range is independent of pH. Similarly, K_3 and K_4 values from kinetic and independent equilibrium studies are in agreement.[8] Other water soluble porphyrins such as the disulfonated deuteroporphyrin dimethyl ester,[10] tetrakis(*N*,*N*,*N*-trimethyl-4-anilinium)porphyrin (H_2–TAP),[11,12] 5-phenyl-10,15,20-tris(*N*-methyl-4-pyridyl)porphyrin,[13] and uro-, copro-, and deuteroporphyrins[14] all react with metals only in the free-base form. Also, the water insoluble 5-(*N*-methyl-4-pyridyl)-10,15,20-triphenylporphyrin[15] studied in detergent solutions stabilized just the $H_4\text{–}P^{2+}$ and $H_2\text{–}P$ forms, of which only $H_2\text{–}P$ was reactive.

The relative incorporation rates and activation parameters for the M^{2+}/TMpyP(4) reactions are listed in Table I. The 40-fold rate difference between Cu^{2+} and Zn^{2+} arises mainly from a more favorable entropy term for Cu^{2+}, and the same is found for these metals and TMpyP(2). While there seems to be a trend to decreasing incorporation rates paralleling increasing negative entropies, the results are not terribly informative, as expected for a complex reaction sequence.

The mechanism shown in (4)–(7) is suggested to explain aspects of the metal–porphyrin formation process.

$$M(H_2O)_6^{2+} + H_2\text{–}P = (M(H_2O)_6^{2+}\cdots H_2\text{–}P) \quad K_{OS} \qquad (4)$$

$$(M(H_2O)_6^{2+}\cdots H_2\text{–}P) = (M(H_2O)_6\cdots H_2\text{–}P^{*}) \quad K_D \qquad (5)$$

$$(M(H_2O)_6^{2+}\cdots H_2\text{–}P^{*}) \rightarrow (M(H_2O)_5^{2+}\text{—}H\text{–}P^{-}) + H_2O + H^{+} \quad k_r \text{ (slow)} \qquad (6)$$

$$(M(H_2O)_5^{2+}\text{—}H\text{–}P^{-}) \rightarrow \text{products} \quad \text{(fast)} \qquad (7)$$

The outer-sphere complexes formed between porphyrins and divalent ions have been estimated to have K_{OS} values at low ionic strengths[2] from $10^{-2}\ M^{-1}$ for the formally tetrapositive TMpyP(4) to $10^2\ M^{-1}$ for the formally tetranegative tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$). Either porphyrin charge type would approach an effective K_{OS} value of ca. 3 M^{-1} at high ionic strengths. The suggestion that porphyrins deform to provide coordination positions for protons[16] or metal ions[17] is evidenced by kinetic studies of the TMpyP(4) protonation process:[18] eq 8–10.

$$H_2\text{–}P = H_2\text{–}P^{*} \quad k_1,\ k_{-1},\ K_D \qquad (8)$$

$$H^{+} + H_2\text{–}P^{*} = H_3\text{–}P^{+} \quad k_2,\ k_{-2} \qquad (9)$$

$$H^{+} + H_3\text{–}P^{+} = H_4\text{–}P^{2+} \quad \text{(very fast)} \qquad (10)$$

The rate constant k_1 for producing the deformed porphyrin ($H_2\text{–}P^{*}$) is $4.6 \times 10^7\ s^{-1}$ at 25 °C, and with $k_{-1} = 1.2 \times 10^9\ s^{-1}$, $K_D \simeq 4 \times 10^{-2}$. The rate-determining step postulated for porphyrin metalation, k_r, involves a dissociative loss of a water molecule from the metal, k_E, and a central proton from the porphyrin, k_{NH}. Thus k_r should approximate the product k_EK_{NH}.

Free base porphyrins are extremely weak bases, and the $H_2\text{–}P$ form for most porphyrins remains as such in molar aqueous hydroxide solutions. The hydroxide ion dependence observed for various porphyrins reacting with zinc in basic solution can be mainly ascribed to the $H_2\text{–}P/Zn(OH)_3^-$ reaction.[19] The equilibrium constant for the $Zn(OH)_3^- + OH^- = Zn(OH)_4^{2-}$ process can be determined from such data,[14] and no effect of hydroxide in labilizing the porphyrin free base protons is noted. The very basic sodium hydroxide/toluene/Me_2SO mixtures have been used to produce monoanion porphyrins from *N*-methylporphyrins and dianions from octaethylporphyrin or etioporphyrin.[20] Under such conditions, the pK_a for the process

$$H_2\text{–}P = H\text{–}P^{-} + H^{+} \quad k_{NH},\ k_f,\ K_a \qquad (11)$$

might be greater than 18. If $K_a = 10^{-18}$ and if the reverse protonation reaction has $k_f = 5 \times 10^{10}\ M^{-1}\ s^{-1}$ (similar to k_2 in eq 9 for the protonation[18] of $H_2\text{–}P^{*}$), then k_{NH} is of the order of magnitude of $10^{-7}\ s^{-1}$. The observed specific metalation constant k_I would according to this scheme be

$$k_I = K_{OS}K_Dk_Ek_{NH} \qquad (12)$$

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Table II. Comparison of Metal–Porphyrin Incorporation Rates for Various Porphyrins with Metal Ion/Water Exchange Rate Constants

porphyrin	metal ion	k_I,[a] $M^{-1}\,s^{-1}$	k^{Cu}_I/k^M_I	k_E,[b] s^{-1}	k_I/k_E, M^{-1}
TMpyP(4)[c]	Cu^{2+}	7.0×10^{-1}	1	2×10^9	4×10^{-10}
	Zn^{2+}	1.6×10^{-2}	44	3.2×10^7	5×10^{-10}
	Co^{2+}	1.1×10^{-3}	693	2×10^6	6×10^{-10}
	Ni^{2+}	2.1×10^{-6}	352000	2×10^4	1×10^{-10}
$TPPS_4$[d]	Cu^{2+}	1.6×10^2	1	2×10^9	8×10^{-8}
	Zn^{2+}	2.9×10^0	55	3.2×10^7	9×10^{-8}
	Co^{2+}	7×10^{-2}	2300	2×10^6	3×10^{-8}
	Ni^{2+}	8.6×10^{-4}	187000	2×10^4	4×10^{-8}
etio[e]	Cu^{2+}	2.1×10^{-1}	1	2×10^9	1×10^{-10}
	Cd^{2+}	1.7×10^{-2}	12	1.6×10^8	1×10^{-10}
	Zn^{2+}	5.0×10^{-3}	42	3.2×10^7	2×10^{-10}
N-methyletio[f]	Cd^{2+}	1.1×10^3		1.6×10^8	7×10^{-6}
	Zn^{2+}	5.0×10^2		3.2×10^7	2×10^{-5}

[a] At 25 °C. [b] k_E is the water-exchange rate constant; from ref 4. [c] TMpyP(4) is tetrakis(*N*-methyl-4-pyridyl)porphyrin; 25 °C, pH 3.0, $(NO_3^-) = 0.5$ M; this paper. [d] $TPPS_4$ is tetrakis(4-sulfonatophenyl)porphyrin; pH 5.4 acetate buffer, 25 °C; see ref 21. [e] etio is etioporphyrin I; DMF solvent, 25 °C; see ref 17. [f] *N*-methyletio is *N*-methyletioporphyrin I; same conditions as for etio; ref 17.

As previously demonstrated,[8,21] the metal–porphyrin incorporation rates, k^M_I, for a given metal ion parallel the corresponding water-exchange rate constant, k_E. For TMpyP(4), the rate ratios k^{Cu}_I/k^M_E are 1:44:700:350 000 for Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}. Equation 12 predicts that the ratio k^M_I/k^M_E should be constant for the same porphyrin with different metals, to a first approximation, and Table II shows that this ratio varies by about a factor of 6 for TMpyP(4). The same relative consistency is also found for this ratio with metals and $TPPS_4$, etioporphyrin I, and *N*-methyletioporphyrin I (Table II).

The porphyrin formation rates should depend on electrostatic parameters in terms of K_{OS}. This might rationalize (Table II) why the tetranegative $TPPS_4$ reacts faster with metals than the tetrapositive TMpyP(4). It is noted that the ratios of the Zn^{2+}–porphyrin formation rates in water of the octa-, tetra-, and dinegatively charged uro-, copro-, and deuteroporphyrins are 10:5:1, respectively.[14] For the same porphyrin charge types, the iron(II)–porphyrin formation rates in water/pyridine media are in the ratios 420:10:1. However, with synthetic uncharged meso-substituted porphyrins[6] or modified uncharged natural porphyrin esters,[23] studied in DMF solutions, the metalation rates are fairly independent of the identity of the porphyrin, indicating a similarity in their K_{OS} and k_{NH} values. The fact that predeformed *N*-methyletioporphyrin I[17] incorporates metal ions 10^5 times faster than etioporphyrin I itself argues for larger K_D and k_{NH} for the *N*-methylporphyrin. Such N-alkylated porphyrins have in fact been shown to be more acidic toward NH dissociation than the corresponding unmethylated porphyrin.[20] In addition, small deuterium isotope effects of 2.2 $(Zn/TPPS_4)$,[24] 2.4 (Zn/TAP),[11] and 1.3 $(Cu/TPPS_4)$[21] have been reported, a possible indication of NH involvement in the activated complex.

Finally, the product $K_{OS}K_Dk_Ek_{NH}$ is certainly of the right order of magnitude to account for the rates of porphyrin metalation. The inclusion of other preequilibria such as the dissociation of one additional water molecule from the metal before the simultaneous final water-proton dissociation reaction would add another k_E/k_{-E} term to the rate law. Assuming weak bonding between the porphyrin and the metal ion, we might expect that k_E/k_{-E} would have values from 10^{-1} to 1.

The inclusion of the notion of a slow N–H central-proton dissociation partially accounts for the slowness of metal–porphyrin reactions, compared to normal ligation processes. This has been suggested earlier by other workers using water-soluble metallophthalocyanine systems,[25] which apparently behave somewhat differently from porphyrins in their metalation reactions. Also, a metal ion independent term in the rate law for the formation of magnesium porphyrins was ascribed to the possible rate limiting monoanion porphyrin rearrangement.[26]

Many metalloporphyrin/metal ion exchange reactions do not involve the dissociation of the porphyrin N–H bond. For example, in the reaction

$$\text{Cd–P} + Zn^{2+} \rightarrow \text{Zn–P} + Cd^{2+} \qquad (13)$$

studied in pyridine at 25 °C, the exchange rates were about a 1000 times faster than those of the corresponding $Zn^{2+}/H_2\text{–P}$ reactions, another possible indication of the rate limiting character of the N–H dissociation.[27] The metals found in geochemical porphyrins might involve transmetalation reactions rather than reactions with free base porphyrins themselves.

It must be noted that each porphyrin has rather specific and peculiar properties. Most synthetic[28] and natural porphyrin[29,30] derivatives dimerize and polymerize in aqueous solution, as a function of pH and ionic strength. Often porphyrins have such high pK_3 values such that the free base form is stable at pH values where most metal ions are hydrolyzed. The favorably low pK_3 of TMpyP(4) is counterbalanced by the strong dependence of its reactions on ionic strength and the ease of reduction of its free base form.[7,31] In addition, the tetrapositive H_2-TAP[11,12] behaves in many of its reactions more like the tetranegative $TPPS_4$ than the tetrapositive TMpyP(4). Such phenomena make comparisons between porphyrins difficult.

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Registry No. $Cu(H_2O)_6^{2+}$, 14946-74-8; $Zn(H_2O)_6^{2+}$, 15906-01-1; $Co(H_2O)_6^{2+}$, 15276-47-8; $Ni(H_2O)_6^{2+}$, 15365-79-4; TMpyP(4), 38673-65-3.

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An Equilibrium and Kinetic Study of Water-Soluble Cadmium Porphyrins

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The equilibrium between many metal ions and porphyrin molecules to form metalloporphyrins in aqueous solution is usually represented by the equation

$$M^{2+} + H_2P = MP + 2H^+ \quad K_e^M \qquad (1)$$

To date, only one complete mass law study of this reaction