

a destabilization of the lone pairs is associated with the stabilization of the b_1 MH_3 bonding orbitals. We believe the small *net* destabilizations of the lone pairs of $(SiH_3)_2O$ and $(SiH_3)_2Se$ are caused by the stabilizing interactions being less than the destabilizing interactions.

A question remains: What orbital interactions are responsible for the lone-pair stabilizations observed for $N(SiH_3)_3$, $N[Si(CH_3)_3]_3$, $NH[Si(CH_3)_3]_2$, and $(SiH_3)_2S$ (and believed likely for $(SiH_3)_3O$ and $(SiH_3)_2Se$)? The traditional opinion, toward which we are inclined, is that the empty $d\pi$ orbitals of the silicon atoms interact with the $p\pi$ lone-pair orbital, causing the stabilization of the latter orbital and an effective drift of the electron density to the silicon atoms. However, it has been suggested that the lone-pair stabilization in compounds of the type R_2N-SiX_3 and $RO-SiX_3$ is due to interaction of the lone pair with the σ^* orbitals of the Si-X bonds.^{15,16} Even though the unperturbed lone pair is assumed to be closer in energy to the σ level than to the σ^* level of the Si-X bonds, it is argued that, because of the Si^+-X^- polarization of the Si-X bonds, the p-orbital coefficient of silicon is greater in the σ^* orbital than in the σ orbital. The resultant greater overlap with the σ^* orbital is believed to overcome the greater energy difference and to account for the stabilization of the lone pair. It is difficult if not impossible to refute this argument with experimental data. However, we believe that the small Pauling electronegativity difference between silicon and carbon ($\Delta\chi = 0.7$), and especially between silicon and hydrogen ($\Delta\chi = 0.3$), would not cause the silicon coefficient to be much greater in σ^* than in σ . Our conclusion is that the lone pairs in the silyl compounds of this study are stabilized by interaction with the silicon d orbitals and destabilized by interaction with the σ Si-H or σ Si-C orbitals, although a significant stabilization by interaction with the σ^* Si-H or σ^* Si-C orbitals cannot be ruled out.

Experimental Section

Trisilylamine was prepared by the reaction of SiH_3Br and NH_3 .¹⁷ The vapor pressure (109 mm at 0 °C) and infrared spectrum of the product agreed with the literature.^{17,18} Tris(trimethylsilyl)amine was obtained commercially (Petrarch) and was sublimed before use.

Vapor-phase X-ray photoelectron spectra were obtained with a GCA McPherson ESCA-36 spectrometer with a Mg anode. The method used for obtaining and calibrating spectra has been described previously.¹⁹ The flow of trisilylamine vapor into the spectrometer was regulated with a needle valve. Tris(trimethylsilyl)amine was not sufficiently volatile to flow through a needle valve and was introduced into the spectrometer through a large-diameter (1.5 cm) inlet system from a reservoir held at -20 °C.

The following data were obtained but not reported in Table I: full widths at half-maximum (fwhm) of the N 1s lines, 1.33 (9) eV for $N(SiH_3)_3$ and 1.47 (9) eV for $N[Si(CH_3)_3]_3$; Si 2p binding energies, 107.47 (3) eV with a fwhm of 1.63 (7) eV for $N(SiH_3)_3$ and 106.34 (3) eV with a fwhm of 1.66 (8) eV for $N[Si(CH_3)_3]_3$; C 1s binding energy, 289.60 (3) eV with a fwhm of 1.61 (9) eV for $N[Si(CH_3)_3]_3$.

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Registry No. $N(SiH_3)_3$, 13862-16-3; $N[Si(CH_3)_3]_3$, 1586-73-8; $NH[Si(CH_3)_3]_2$, 999-97-3; $(SiH_3)_2O$, 13597-73-4; $(SiH_3)_2S$, 16544-95-9; $(SiH_3)_2Se$, 14939-45-8.

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Does Coordination Activate Heterocycles toward Nucleophilic Attack? The Importance of π Interactions between Metal Ion and Ligand

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Transition-metal complexes containing coordinated nitrogen heterocycles have been prominent in the chemical literature for a variety of reasons including their photochemical properties, substitution inertness, and stabilization of low oxidation states. The interest in these complexes has resulted in much, and often lively, debate in the chemical literature on whether or not metal ions activate coordinated heterocycles toward nucleophilic attack.¹⁻⁷ Evidence for covalent hydration and pseudobase formation in many chemical processes, including nucleophilic substitution, has been collected.^{1,4} Two recent reviews^{2,3} have evaluated this evidence and concluded that, in general, alternative explanations are more appropriate, although controversy still remains for some systems.⁴ The purpose of this note is to question the chemical basis for whether coordination may be considered in the same way as quaternization with regard to activation of heterocycles (which is the basis of Gillard's^{1,4} mechanisms). This fundamental question has been largely ignored in the considerable discussion in this area.

The fundamental difference between quaternization of a nitrogen heterocycle by an alkyl group and coordination by a metal ion is the interaction of metal d orbitals with the ligand π systems. In essence, the metal ion acts not only as an electron-withdrawing σ group (as does R^+) but also as a π donor and a π acceptor (resonance effects) through its d orbitals. Reduction of electron density within the heterocycle by σ acceptance and π acceptance by the metal ion will polarize the $N=C$ bonds, activating them toward nucleophilic attack. Opposing this process is metal ion π donation, which deactivates the ligand. Clearly, a predominance of one of these factors will result in activation or deactivation of covalent hydration or pseudobase formation. In order to set a background for discussion, the factors which affect π bonding and π back-bonding will be briefly outlined below.

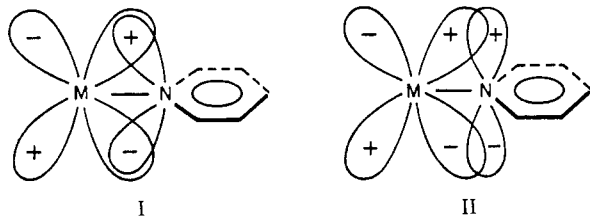
(i) The π -donating and π -accepting abilities of a given metal ion depend on the relative energies of the metal d orbitals as compared to the lowest lying interacting π^* and highest energy interacting π orbital.

(ii) Both interactions are increased as the extent of orbital overlap increases.

(iii) Electronic configurations with six or more outer-shell d electrons will be good π donors while π acceptance by the metal ion will increase as the outer-shell d-electron density decreases.

We will initially consider point i. As the difference in energy of the π^* and d orbitals decreases, their interaction increases, leading to stronger π donation by the metal ion and weaker π acceptance.^{8,9} Therefore, π back-bonding is more favored as you go down a transition-metal triad and as you decrease the oxidation state. In consideration of point ii, a factor overlooked is that geometrical orbital overlap is inherently greater for interactions involving π^* orbitals (I) than for those involving π orbitals (II) (as shown for pyridine). Therefore, π back-bonding is more favored than is π bonding. Secondly, the strengths of interaction for both I and II will increase with

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the radial extension of the d orbitals, for a given ligand. This factor leads to increased interaction down a transition-metal triad and with a decrease in oxidation state. Point iii means that π donation by the metal ion (and hence ligand deactivation) will increase with decreasing oxidation state and will be greater for elements to the right of the periodic table. We are now in a position to make definite statements as to where we are most likely to find activation of heterocycles on coordination. First-row transition elements in high oxidation states toward the left of the periodic table are most likely to bring about activation due to π effects. Activation by σ polarization of the C=N bond should follow similar trends, since it is dependent on both the effective charge:radius ratio and the d-electron density.

Now that an order of activation has been established, the reactivity of nonaromatic unsaturated ligands coordinated to metal ions will be used to ascertain the importance of metal ion activation. In this regard, it is instructive to consider available data on the activation/deactivation of coordinated imines and nitriles by metal ions of the Co and Fe triads.⁸⁻¹³ While simple acyclic imines coordinated to Co(III) may be attacked by nucleophiles,¹⁰⁻¹² they are remarkably stable in comparison to iminium ions. It has been argued that this observation is consistent with weaker polarization by Co^{3+} , as compared to that by a proton (or alkyl group).^{10,11} It is also likely that there is a degree of stabilization by π back-bonding, and more recent work on the hydrolyses of acetonitrile shows a small effect on rate constants, presumably due to a small increase in π back-bonding in going down the cobalt triad.¹³ Since *N*-methylpyridinium does not undergo covalent hydration or pseudobase formation,^{2,3,14-16} it is clear from the reactivity of coordinated imines that pyridine coordinated to Co(III) will be much less reactive. Deactivation by other d^6 ions in comparison to quaternization would follow the order $\text{Co(III)} < \text{Rh(III)} < \text{Ir(III)} < \text{Fe(II)} < \text{Ru(II)} < \text{Os(II)}$. For the latter three ions, the importance of metal ion π donation in causing deactivation of ligands is well-known.^{8,9} These effects are expected to be more prominent for the d^8 complexes of Ni(II), Pd(II), and Pt(II). Therefore, all of these metal ions would deactivate heterocycles toward nucleophilic attack in comparison to quaternization by alkyl groups, in agreement with recent assessments of the experimental data.^{2,3,5-7} Complexes of the d^6 Pt(IV), d^5 Fe(III), Ru(III), and Os(III), and

d^3 Cr(III) ions remain as possibilities for observing covalent hydration and pseudobase formation, and this is the general area where some controversy still exists.⁴ Pt(IV) has the highest ratio of charge:radius and is, therefore, the strongest σ polarizer of the ions under consideration. However, $[\text{Pt}(\text{py})_4\text{Cl}_2]^{2+}$ ⁴ (where there is still controversy as to whether or not nucleophilic attack occurs at the ligand) has its charge somewhat neutralized by the negative Cl^- ligands. These ligands also direct electron density into the π^* orbitals of the pyridine ligands through the d orbitals of the metal ion. Therefore, activation of the pyridine ligands is either comparable to or less than that for d^6 Co(III) ions, and there is no basis for expecting nucleophilic attack at the ligand in this instance.

There are strong indications that the M(III) ions of the iron triad strongly activate ligands toward nucleophilic attack,^{8,9,17} although such reactions may be complicated by base-catalyzed disproportionation,¹⁸ in which the M(IV) state is active. Fe(III) and Ru(III)^{8,9,17} (but not Os(III))^{19,20} are poor π donors and good candidates for activating coordinated heterocycles and d^3 Cr(III) is even more so, giving an activation order of $\text{Ru(III)} < \text{Fe(III)} < \text{Cr(III)}$. However, nucleophilic attack at the ligand has to compete with other possible chemical reactions, such as deprotonation at the 3- and 3'-positions of the coordinated 2,2'-bipyridine ligands, and with direct attack at the metal ion to form a seven-coordinate species.^{2,3,5-7} Clearly, the electron-deficient metal centers undergo nucleophilic addition more readily to form complexes of increased coordination number and also impart greater acidity to the bipyridine ligands. It has been pointed out elsewhere³ that the data available for Cr(III) indicate strongly that nucleophilic attack at the metal ion is more favored than attack at the ligand. One of the remaining pieces of evidence that Gillard⁴ uses in support of covalent hydration is centered on complexes of the type $[\text{Fe}(\text{LL})_3]^{3+}$, which are very stable when the activity of water is reduced to zero. However, similar reactivity patterns are observed for substitution of NH_3 in $[\text{Ru}(\text{NH}_3)_6]^{3+}$.²¹ The most plausible explanation we can find for this result is that water acts as a nucleophile to form a seven-coordinate intermediate, and this is also likely for Fe(III).^{21,22} This proposition of a seven-coordinate intermediate is also strongly supported by the crystallographic work on the Fe(III) complex $[\text{Fe}(\text{edta})(\text{OH}_2)]^-$,²³ where water acts as a seventh ligand. It is apparent that for such systems direct nucleophilic attack at the metal is more favored than attack at the ligand, despite the expectation that the ligand may be slightly activated.²²

In summary, qualitative arguments for activation of coordinated heterocycles can only be made for Fe(III), Ru(III), and Cr(III) (of the metal ions under scrutiny). However, these metal ions are also the most efficient at activating the ligands toward competing deprotonation reactions (and subsequent chemistry) and direct nucleophilic attack at the metal ion. All the experimental evidence so far available, and the new discussion and evidence brought forward here, shows that, except for activated ligands, nucleophilic attack at coordinated heterocycles does not occur. The basic premise that coordination can be considered in the same manner as quaternization is

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incorrect, as such a premise fails to take account of the weaker σ polarization brought about by coordination and also fails to take account of π back-bonding deactivation, which is inherently greater than π -bonding activation.

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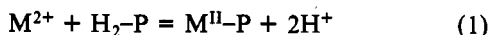
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Equilibrium Constants and Electrophilic Exchange Reaction Kinetics of Lead(II) Porphyrins

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Although over 50 metal ions react with free-base (H_2 -P) porphyrins to form metalloporphyrins (M-P),¹ equilibrium constants for these reactions have been measured only in the cases of Zn^{2+} , Cd^{2+} , and Hg^{2+} . Zinc(II)² and cadmium(II)³ produce 1:1 metal to porphyrin species (eq 1), while 1:1, 2:1,



and 3:2 adducts have been demonstrated for $Hg(II)$.⁴⁻⁷ Such reversible equilibria allow for detailed kinetic studies of electrophilic exchange reactions, where one metal can displace another from its porphyrin complex. A number of exchange studies have been run in nonaqueous media,⁸⁻¹¹ while only cadmium^{7,12} and zinc^{10,13,14} porphyrins have been examined in aqueous solution.

We report equilibrium and rate constants for lead(II) reactions with water-soluble porphyrins and the kinetics of the exchange of Zn^{2+} and Co^{2+} with lead and cadmium porphyrins. Since high concentrations of zinc protoporphyrin are found in individuals with lead poisoning,¹⁵ the facile $Zn^{2+}/Pb^{II}-P$ exchange reactions might be one possible pathway for the production of this complex in vivo.

Experimental Section

The porphyrins tetrakis(*N*-methyl-4-pyridyl)porphyrin (H_2 -TMPyP(4)), its 2-pyridyl analogue (H_2 -TMPyP(2)), and tetrakis(*N,N,N*-trimethyl-4-aniliniumyl)porphyrin (H_2 -TAP) prepared before³ were converted by ion-exchange techniques into their nitrate salts. The transition-metal nitrates were analyzed by EDTA titrations.¹⁶ All reactions were run at 25 °C, at an ionic strength of 0.2 (NaNO₃),

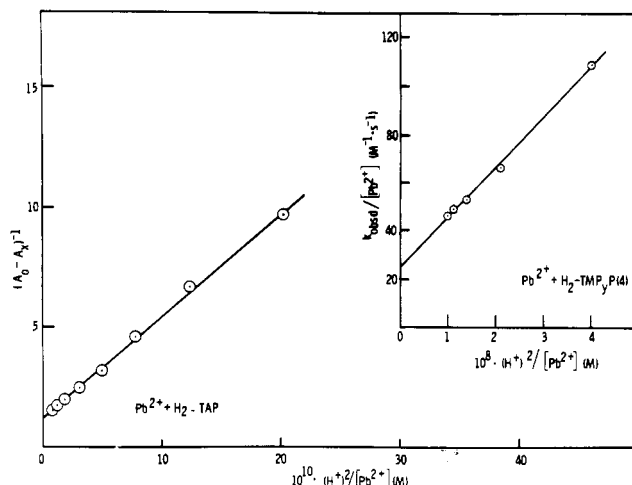


Figure 1. Left side: Graphical determination of the equilibrium constant K_{Pb} for the Pb^{2+}/H_2 -TAP reaction, from eq 3. Inset: Plot of $k_{obsd}/[Pb^{2+}]$ vs. $[H^+]^2/[Pb^{2+}]$ for the approach to equilibrium of the Pb^{2+}/H_2 -TMPyP(4) reaction.

Table I. Equilibrium and Formation Rate Constants for Metalloporphyrins at 25 °C

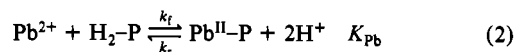
porphyrin	pK_3^a	K_{Pb}^b (k_{Pb}) ^{b,c}	$K_{Cd}^{b,d}$ (k_{Cd}) ^{b,d}	$K_{Zn}^{b,e}$ (k_{Zn}) ^{b,e}
H_2 -TMPyP(2)	-0.9	9.5×10^{-8} (20)	7.9×10^{-7} (7)	1.9×10^2 (4.9×10^{-4})
H_2 -TMPyP(4)	+1.4	3.2×10^{-8} (28)	2.0×10^{-8} (40)	4.4 (3.7×10^{-2})
H_2 -TAP	+3.6	3.0×10^{-10} (128)	1.7×10^{-10} (87)	

^a pK_3 for the H_3 -P⁺/ H_2 -P reaction; see ref 3. ^b K_M in units of M; k_M in units of $M^{-1} s^{-1}$. ^c This paper. ^d Data from ref 3.

^e Data from ref 2.

with 1×10^{-2} M 4-morpholineethanesulfonic acid (MES) as the buffer.

Formation Constants. The lead porphyrin formation constants (eq 2) were studied between pH 4 and 6.2, with total lead concentrations less than 10^{-3} M. This pH range avoids $PbOH^+$ ($pK_a = 7.7$)¹⁷ and



is such that the porphyrins are in their free-base states.³ The low lead levels ensure that Pb^{2+} (rather than polynuclear¹⁷ $Pb_2(OH)^{3+}$ or $Pb_4(OH)_4^{4+}$) is the reactant.

At pH 4 with ca. 10^{-6} M H_2 -TMPyP(4) and 1×10^{-4} M Pb^{2+} , the typical free-base spectrum of the porphyrin is observed. As the pH is raised, Pb^{II} -TMPyP(4) appears, with bands at 476 nm ($\epsilon 1.5 \times 10^3$), 609 nm ($\epsilon 9.7 \times 10^3$), and 660 nm ($\epsilon 1.4 \times 10^4$). Isobestic points are found at 390, 445, 590, and 503 nm, indicating that H_2 -P and Pb^{II} -P are the only absorbing species. This porphyrin spectrum is similar to those of Pb^{II} -TMPyP(4) (containing an impurity) reported by Harriman and co-workers¹⁸ ($\lambda_{max} = 469, 606,$ and 658 nm) and lead(II) tetraphenylporphyrin in benzene ($\lambda_{max} = 467, 607,$ and 657 nm). With pHs higher than 6.5, lead in the 10^{-4} M concentration range precipitates.

At 424 nm, the Soret peak for H_2 -TMPyP(4), we can define A_0 as the absorbance of H_2 -P, A_{00} as that of Pb^{II} -P, and A_x as the absorbance of mixtures of the two species. The solution is buffered, and with $[Pb^{2+}]_0 \gg [H_2-P]_0$, then $[Pb^{2+}]_0 = [Pb^{2+}]$. It¹⁹ has been shown that K_{Pb} for eq 2 can be derived from linear graphs of $(A_0 - A_x)^{-1}$ vs. $[H^+]^2/[Pb^{2+}]$, from eq 3. Such a plot for the Pb^{2+}/H_2 -TAP

reaction is shown in Figure 1, and the resulting equilibrium constants are listed in Table I. The same K_{Pb} values could be obtained from

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