Table II

Metalloporphyrin	$10^{-4}\epsilon$ (550 nm)	σ_X[a]	log K
Zinc tetra(4-methoxyphenyl)porphine	2.52	−0.268	3.690 ± 0.002
Zinc tetra(4-methylphenyl)porphine	2.37	−0.170	3.721 ± 0.009
Zinc tetra(3-methylphenyl)porphine	2.48	−0.069	3.798 ± 0.032
Zinc tetraphenylporphine	2.30	0	3.724 ± 0.014 3.78 ± 0.02[b] 3.70[c]
Zinc tetra(4-fluorophenyl)porphine	2.13	0.062	3.907 ± 0.018
Zinc tetra(3-methoxyphenyl)porphine	2.30	0.115	3.844 ± 0.021
Zinc tetra(4-chlorophenyl)porphine	2.38	0.227	4.043 ± 0.025
Zinc tetra(3-fluorophenyl)porphine	1.98	0.337	4.087 ± 0.004
Zinc tetra(3-chlorophenyl)porphine	2.44	0.373	4.141 ± 0.005
Zinc tetra(3-bromophenyl)porphine	2.31	0.391	4.192 ± 0.005

[a] L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill, New York, N.Y., 1970, p 356. [b] Data from ref 10. [c] Calculated from the data of ref 9.

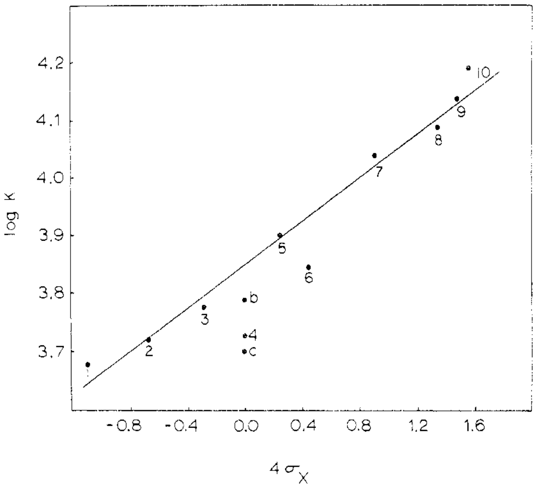

Figure 1. Plot of log K vs. σ_X: 1, p-OCH_3; 2, p-CH_3; 3, m-CH_3; 4, b, c, H; 5, p-F; 6, m-OCH_3; 7, p-Cl; 8, m-F; 9, m-Cl; 10, m-Br. See Table II.

series because metal to ligand π back-bonding is the more important means of electron delocalization in metalloporphyrins.[4d] The d orbitals of Zn(II) are completely filled and thus it is expected that the Zn(m- or p-X)TPP series will be more sensitive to change in peripheral groups than the VO(p-X)TPP series because the lone d electron is in the d_{xy} orbital in the case of V(IV)[11] and cannot interact with the π^* system of the porphyrin ring.[4d] The work of Hoard and coworkers has shown that the Zn atom lies out of the plane of the porphine skeleton[12] and hence the $d\pi$–$L\pi^*$ overlap may be considerably reduced in comparison to that of the Ni system. This reduced overlap may partially account for the Zn(m- or p-X)TPP series being less sensitive to change in peripheral groups than the Ni(m- or p-X)TPP series. Similarly, it has been found that zinc porphyins are less sensitive to substituent changes than the nickel porphyrins for the substituted 2,4-deuteroporphyrin system.[4a]

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Registry No. Zn(p-OCH_3)TPP(py), 57304-76-4; Zn(p-CH_3)TPP(py), 57304-77-5; Zn(m-CH_3)TPP(py), 57304-78-6; ZnTPP(py), 24389-79-5; Zn(p-F)TPP(py), 57304-79-7; Zn(m-OCH_3)TPP(py), 57304-80-0; Zn(p-Cl)TPP(py), 57304-81-1; Zn(m-F)TPP(py), 57304-82-2; Zn(m-Cl)TPP(py), 57304-83-3; Zn(m-Br)TPP(py), 57304-84-4; Zn(3,5-di-OCH_3)TPP(py), 57304-85-5; Zn(3,4-di-Cl)TPP(py), 57379-35-8.

Supplementary Material Available: Table I containing the spectroscopic data for the zinc porphyrin–pyridine systems (4 pages). Ordering information is given on any current masthead page.

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Oxidation of Trimethylamine by Copper(II) Chloride[1]

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In previous studies[2-4] of the coordination and oxidation of aliphatic amines by copper(II) chloride, key steps in the complex reaction sequence were shown to be

$$CuCl_2 + e^- \rightarrow CuCl_2^- \rightleftharpoons CuCl + Cl^-$$

$$RCH_2CH_2NR_1R_2 \rightarrow 2e^- + 2H^+ + \underbrace{RCH{=}CHNR_1R_2}_{} \longrightarrow \text{polymer}$$

Obviously, dehydrogenation of an alkyl to a (substituted) vinyl group would be impossible with only methyl substituents present, yet conversion of trimethylamine by warm copper(II) chloride to a dark tarry product, presumably by oxidation–reduction, had been observed.[5] Also, in their isobaric temperature–composition study of the copper(II) chloride–trimethylamine system, Simon and co-workers[6] observed the complexes to undergo irreversible thermal decomposition. Recent work by Kiesel and Schram[7,8] on the oxidation of trimethylamine by vanadium(IV) chloride, in which it was shown that the dimethylmethyleneammonium cation plays a key role as an intermediate amine oxidation product, prompted our further investigation of the trimethylamine–copper(II) chloride reaction.

Experimental Section

Materials and Technique These were as described previously.[2-4] Microanalyses were done by Galbraith Laboratories, Knoxville, Tenn.

Instrumentation. A Beckman IR8 spectrophotometer and an F&M 700 gas chromatograph were used. With the latter, fitted with 6-ft stainless steel columns packed with 5% tetraethylenepentamine on Fluoropak 80, authentic samples of mono-, di-, and trimethylamines eluted as a single unresolved sharp peak, cleanly separated from formaldehyde.

Coordination of Trimethylamine by Copper(I) Chloride. A suspension of 14.25 mmol of copper(I) chloride in several milliliters of trimethylamine was stirred magnetically at −22° for 1 week. When the reaction bulb was then attached to the vacuum line and the excess of trimethylamine removed at 0° until the pressure dropped to a negligible value, 14.22 mmol of trimethylamine was retained in the light brown product, $CuCl{\cdot}N(CH_3)_3$; mp 122–124° (sealed tube). Anal. Calcd for $CuClNC_3H_9$: C, 22.79; H, 5.74. Found: C, 22.81; H, 5.82.

Coordination of Trimethylamine by Copper(II) Chloride. Similar removal of trimethylamine at 0° from anhydrous copper(II) chloride gave first a blue-green solid product, presumably $CuCl_2{\cdot}2N(CH_3)_3$, with a considerable dissociation pressure. The further removal of amine until the pressure dropped to a negligible value gave a mustard-colored solid, mp 134° dec (sealed tube), of composition $CuCl_2{\cdot}1.081N(CH_3)_3$ based on the gain in weight. Anal. Calcd for this composition: C, 19.64; H, 4.94; N, 7.63; Cu, 32.04. Found: C, 19.76; H, 5.09; N, 7.69; Cu, 31.92. $\mu_{eff} = 1.79$ BM (Gouy method, room temperature).

Oxidation of Trimethylamine by Copper(II) Chloride. Anhydrous copper(II) chloride, in a vacuum-line reaction bulb, was heated in contact with an exactly equimolar amount of trimethylamine gas. As the temperature rose above about 75°, the gas pressure dropped sharply and a black tarry solid product was formed. The gain in weight corresponded to the consumption of 0.96 mol of trimethylamine/mol of original copper(II) chloride. Water was condensed onto the product, the mixture was stirred for several hours at room temperature, and the most volatile portion of the mixture was then condensed into another bulb on the vacuum line and removed for qualitative tests.

In other experiments, trimethylamine vapor at a pressure of 687 Torr, in equilibrium with liquid trimethylamine in a reservoir at 0°, was allowed to contact solid copper(II) chloride at about 85° in a vacuum-line reaction bulb for several hours. The bulb was then cooled to 0° and an excess of trimethylamine was condensed onto the dark reaction product. The mixture was stirred, and subsequently the excess of trimethylamine was removed until the pressure dropped to a negligible value. Based on the gain in weight, the dark red tarry product contained 1.2–1.4 mol of trimethylamine/mol of copper(II) chloride, on an original basis. Ir (cm^{-1}): 3150–2700, 2480, 1690, 1600, 1048, 1015, 980, 825.

Results

Copper(I) chloride is coordinated by trimethylamine at 0° to give the complex $CuCl{\cdot}N(CH_3)_3$, which has a negligible dissociation pressure at room temperature and darkens rapidly on exposure to air. Copper(II) chloride is coordinated by trimethylamine to give a stable yellow-brown normally paramagnetic complex of composition $CuCl_2{\cdot}N(CH_3)_3$. There is also a blue-green higher complex with a considerable dissociation pressure at 0°.

Above about 75°, trimethylamine is irreversibly oxidized by copper(II) chloride. The somewhat variable reaction stoichiometry is in the range of about 1.0–1.4 mol of trimethylamine bound/mol of copper(II) chloride (original basis), depending on whether trimethylamine is in excess during the reaction. The ir spectrum of the dark tarry product contains features characteristic of the trimethylammonium and the dimethylmethyleneammonium cations. Hydrolysis of the reaction mixture gives dimethylamine (identified by the Hinsberg test), formaldehyde (identified by gas chromatography), copper(I) chloride and chloride ion (identified by aqueous qualitative tests), and a dark tar.

Discussion

The results on the complexes of trimethylamine with copper(I) chloride and copper(II) chloride are not in agreement with those of Peters[9] and of Simon and co-workers,[6] respectively. Peters found no complex in the copper(I) system, presumably because of insufficient time for reaction. Simon and co-workers found a series of complexes in the copper(II) system, and from their isobaric temperature–composition diagram it can be seen that at 0° and 20 Torr a complex $CuCl_2{\cdot}nN(CH_3)_3$ (where n is at least 2) should be the stable species. We find the dissociation pressure of such a complex at 0° to be an order of magnitude higher. The complex $CuCl_2{\cdot}N(CH_3)_3$ has been prepared previously by crystallization from a solution of the components in methanol.[10]

Scheme I

$$2CuCl_2 + 2(CH_3)_3N \rightarrow 2[CuCl_2{\cdot}N(CH_3)_3]$$

$$2CuCl_2 + 2e^- \rightarrow 2CuCl + 2Cl^-$$

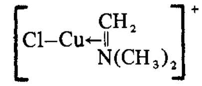
$$(CH_3)_3N \rightarrow (CH_3)_2N{=}CH_2^+ + H^+ + 2e^-$$

$$(CH_3)_3N + H^+ \rightarrow (CH_3)_3NH^+$$

$$\begin{aligned}2CuCl_2 + 2(CH_3)_3N \rightarrow 2[CuCl_2{\cdot}N(CH_3)_3] \rightarrow 2CuCl +\\ (CH_3)_2N{=}CH_2^+Cl^- + (CH_3)_3NH^+Cl^-\end{aligned}$$

The oxidation of trimethylamine by copper(II) chloride much resembles its oxidation by vanadium(IV) chloride.[7,8] Formation of the dimethylmethyleneammonium cation, $(CH_3)_2N{=}CH_2^+$, is indicated especially by the 1690-cm^{-1} absorption; $\nu_{N=C}$ has been assigned in the 1663–1696-cm^{-1} region in various salts of this cation.[7,8,11,12] Also, its expected[11] hydrolysis products, formaldehyde and dimethylamine, were identified. The reactions involved in the oxidation–reduction can be written as in Scheme I.

The actual state of the reaction products and the variable stoichiometry must be related to the subsequent complex interactions possible, viz., (1) formation of chlorocuprate complex anions, some of whose salts are oils at room temperature,[13] e.g., $CuCl + Cl^- \rightleftharpoons CuCl_2^-$, (2) coordination of copper(I) chloride by (excess) trimethylamine, (3) formation of a cationic π complex between copper(I) chloride and the dimethylmethyleneammonium ion



$$\left[Cl{-}Cu{\leftarrow}\overset{CH_2}{\underset{N(CH_3)_2}{\|}}\right]^+$$

(this complex was claimed by Mason and Rucci,[14] though no characterization was published), and (4) reaction of the dimethylmethyleneammonium ion with (excess) trimethylamine. Kiesel and Schram,[7,8] following Böhme and Haake,[15] wrote for this the reaction

$$(CH_3)_3N + (CH_3)_2N{=}CH_2^+Cl^- \rightarrow (CH_3)_2NCH_2N(CH_3)_3^+Cl^-$$

yet they also reported failure in attempting this reaction with pure starting materials under three sets of experimental conditions. Kiesel and Schram also suggested

$$\begin{aligned}(CH_3)_3N + (CH_3)_2N{=}CH_2^+Cl^- \rightarrow (CH_3)_3NH^+Cl^- +\\ (1/n)((CH_3)_2NCH)_n\end{aligned}$$

and such formation of a polymer seems better in accord with the tarry nature of the reaction product.

Registry No. $CuCl{\cdot}N(CH_3)_3$, 57527-16-9; $CuCl_2{\cdot}N(CH_3)_3$, 57527-17-0; $(CH_3)_3N$, 75-50-3; $CuCl_2$, 7447-39-4; $(CH_3)_2N{=}CH_2^+$, 28149-27-1.

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