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Porous, Polymer-Bonded Metalloporphyrins

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Abstract: The synthesis of a series of porous, polymer-bonded metalloporphyrins is described. Functionalized tetraphenylporphines are attached to porous polystyrene resins via amine, carbonyl, and ester linkages and metal ions are then incorporated into the structures. ESR data for copper derivatives were used to characterize the materials. It was shown that porphyrin polymers which contain both oxidation (cobalt) and proton-acceptor sites (amine or carboxylate groups) are effective catalysts for the oxidation of thiols to disulfides. Factors affecting the deactivation of these catalysts are discussed.

Research into the chemistry of porphyrins and of metalloporphyrins has attracted wide interest. Metalloporphyrins, present in petroleum,[1,2] contribute to undesirable metal contamination in cracking catalysts.[3] Biologically, porphyrins and related structures occur in hemin, chlorophyll, and vitamin B_{12}.[4] In inorganic chemistry, porphyrin and model-porphyrin ligands can provide known and fixed coordination environments for the study of metal ions under a variety of conditions.[5]

Interest in organic semiconductors, heterogeneous catalysis, and immobilized enzyme models has led to the synthesis of three classes of porphyrin-containing polymers, which may be termed (a) coordination polymers, (b) polymer-attached porphyrins, and (c) polyporphyrins. Coordination polymers can be represented by a complex of poly-4-vinylpyridine with cobaloxime, a $\mathbf{B}_{12}$ model, wherein the polymer coordinatively binds to cobalt.[6] Wang has provided an additional example, a coordination polymer in which heme is bonded through iron to a polystyrene-embedded imidazole derivative.[7] Coordination of iron porphyrins to a polystyrene-bonded imidazole was reported by Collman et al.[38,39]

The fact that naturally occurring porphyrins contain pendant carboxylic acid functions[4] has been used in the synthesis of the second group, the polymer-attached porphyrins. By the formation of amide linkages between these acid functions and a polyethyleneimine, Lautsch and coworkers were able to attach both hemin and chlorophyll structures to preformed polymers.[8]

Polyporphyrins, the third group, would include condensation polymers prepared from glycols and difunctional porphyrins such as deutero- and *meso*-porphyrins. The group could further include synthetic materials wherein the polymerization reaction is the formation of the porphyrin itself. Polymeric phthalocyanines are an example of polyporphyrins.[9,10]

All of the above have been dense polymers, polymers whose physical form can be radically affected by solvent. The development of fixed-pore or macroreticular resins, reviewed by Frisch,[11] has added a new dimension to polymer applications. In contrast to the dense materials mentioned above, macroreticular resins substantially retain their shape and porosity in the presence of nonpolar solvents. Such retention of porosity is particularly useful in nonaqueous media, e.g., in the reactions of hydrocarbons over sulfonic acid resin catalysts,[12] in conversion processes catalyzed by resin-bonded transition metal complexes,[13,40,41] and even in ion exchange sequences over chelating, macroreticular resins.[14] One purpose of the paper will be to describe the synthesis of fixed-pore or macroreticular polymer-bonded porphyrins.

A second purpose will be to characterize the resultant polymers, i.e., to show that polymers can be prepared which contain a high, and perhaps "monomolecular", dispersion of porphyrin moieties. Such a dispersion of porphyrins and of porphyrin analogs would distinguish these polymeric species from the monomers. Porphyrin monomers commonly aggregate in solution, a factor of considerable biological significance.[15,16]

To provide an example of the possible utility of these porphyrin polymers is the third purpose, said example being related to the removal of mercaptan sulfur compounds from cracked gasolines (sweetening). Porphyrins and phthalocyanines, and particularly the sulfonate or carboxylate derivatives thereof, are useful thiol oxidation catalysts.[17,18]

Finally, the potential utility of these polymers in other porphyrin applications, such as B_{12} chemistry,[19,20] is noted.

Experimental Section

Materials. Resin starting materials were obtained from Rohm and Haas and from Ionac. All were porous, macroreticular, styrene-based polymers, cross-linked with divinylbenzene (DVB) or with ethylene glycol dimethacrylate. For the synthesis of ionically bonded porphyrins, an anion exchange resin was used, A-26, a polymeric trimethylbenzylammonium species, in its chloride, acetate, or hydroxide form. Covalent attachment of porphyrins proceeded either from an unsubstituted polystyrene such as XAD-2 (DVB cross-linked, 300 m^2/g surface area) or from its chloromethylated derivative. The latter materials were intermediates in the commercial production of anion exchange resins and contained about 17% chlorine by weight. Laboratory-scale chloromethylation of cross-linked polystyrenes can be effected by the use of chloromethyl methyl ether and a stannic chloride catalyst.[21]

Porphyrins were synthesized from pyrrole and substituted benzaldehydes according to the procedures developed by Adler and coworkers.[22,23] Thus, reaction of 4-carboxybenzaldehyde and pyrrole, each 0.3 *M*, in propionic acid yielded purple crystals of *meso*-tetra(*p*-carboxyphenyl)porphine, TPP-COOH. Anal. Calcd for $C_{48}H_{30}N_4O_8$: C, 72.91; H, 3.79; N, 7.08. Found: C, 72.64; H, 3.80; N, 6.70.

Similarly, reaction of pyrrole with benzaldehyde itself or with *p*-acetamidobenzaldehyde, the latter followed by HCl hydrolysis, yielded tetraphenylporphine, TPP, and *meso*-tetra(*p*-aminophenyl)porphine), $TPP\text{-}NH_2$, respectively.

Polymer-Bonded Porphyrins. Synthesis of a number of resin-bonded tetraphenylporphines is described in the examples below.

Amine Linkage. Ten grams of chloromethylated resin (17% Cl, 0.05 mol of Cl) was added to a solution of 1.0 g of $TPP\text{-}NH_2$ (1.5×10^{-3} mol) in 200 cm^3 of DMF, and the reaction mixture was heated at 100° for 2–3 hr with stirring. After cooling, the resin was filtered and was washed with DMF and 1 *N* HCl, until a colorless filtrate was obtained. The green product polymer, obtained after washing with 0.1 *N* NaOH and water, contained 1.1% nitrogen or about 6% porphyrin. The product polymer had retained 5.2% Cl and was given the designation $Res\text{-}NH\text{-}TPP\text{-}NH_2$.

Ester Linkage. A mixture of 5.0 g of TPP-COOH (6.3×10^{-3} mol) and 50.0 g of porous polybenzyl alcohol resin (obtained by hydrolysis of the chloromethylated material and containing 0.36 mol of OH and 0.14 mol of Cl groups) was refluxed under a Dean–Stark trap in a 1:2 vol/vol DMF–benzene solution containing 0.3% H_2SO_4. Water removal was complete in 6 hr. The green product, washed with DMF and aqueous base and neutralized with 1 *N* HCl, contained 0.2% nitrogen (2–3% porphyrin) and was designated Res-OOC-TPP-COOH. The ir spectrum of the resin revealed a carbonyl stretch at 1690 cm^{-1}, as compared with 1685 cm^{-1} for the parent, TPP-COOH.

Ketone Linkage. Fifteen grams of TPP-COOH (0.019 mol) and 100 cm^3 of thionyl chloride (1.34 mol) were combined in a 1-l. round-bottom flask. When gas evolution subsided, 100 g of XAD-2 resin (about 0.9 mol of benzene rings) and 300 cm^3 of 1,1,2,2-tetrachloroethane were added. The mixture was heated to 130° with stirring to drive off excess $SOCl_2$. After cooling to 10°, 15 g of $AlCl_3$ (0.11 mol) was added, and the mixture was stirred, without further cooling, for 16 hr. The solid was filtered and thoroughly washed with tetrachloroethane, methanol, and aqueous base. After neutralization with 1 *N* HCl, the resin was dried in vacuo at 50°. Nitrogen content of this Res-CO-TPP-COOH polymer was 0.3% (4% porphyrin). A carbonyl stretch was observed in the infrared region at 1670–1680 cm^{-1}.

Metal Derivatives. For the incorporation of metal ions into preformed porphyrins and into porphyrin-containing polymers, the techniques reviewed by Adler and coworkers were employed.[24] To prepare CoTPP-COOH, for example, 6.5 g of TPP-COOH (0.008 mol) and 2.5 g of cobalt acetate (0.01 mol) were refluxed for 3 hr in 700 ml of 1:1 chloroform:acetic acid.[25] The mixture was cooled, filtered, washed extensively with water, and dried in a vacuum desiccator. The visible spectrum of a 10^{-5} *M* solution in DMF exhibited an absorption at 417 mμ, as compared with ~410 mμ for the corresponding Ni, Cu, and Zn compounds in aqueous solution.[15] Anal. Calcd for $C_{48}H_{28}N_4O_8Co$: C, 68.00; H, 3.31; N, 6.61; Co, 6.97. Found: C, 68.74; H, 3.59; N, 6.33; Co, 6.45.

By use of the above techniques, polymer-bonded porphyrins were converted to the corresponding metallo derivatives. Thus, copper and cobalt ions were incorporated into a $Res\text{-}NH\text{-}TPP\text{-}NH_2$ polymer by reaction of excess metal acetate in acetic acid at 100°. After washing with 1 *N* HCl to remove any excess metal ion and careful neutralization with 0.1 *N* NaOH, a resin containing 0.6% nitrogen was found to have added 0.4% copper. A material containing 0.5% nitrogen gained 0.2% cobalt. These analyses correspond to nitrogen/metal mole ratios of 7 and 10, respectively, as compared with a theoretical value of 8.

The tetrasodium salt of the tetrasulfonated cobalt phthalocyanine, Na_4CoPTS, had been synthesized earlier.[26] This material and the sodium salt of CoTPP-COOH were used for the preparation of porphyrin-containing anion exchange resins, examples of porphyrins held ionically in polymers. Simply on mixing solutions of these salts with anion exchange resins, the multiply charged porphyrin anion was observed to displace singly charged anions, even hydroxide.

Instrumentation. Infrared data in Nujol mulls were taken on a Beckman IR-10; visible spectra were taken on a Cary 14. Electron spin resonance (ESR) data were obtained on a Varian Model V-4500, X-band spectrometer with 100 kHz field modulation. Diphenylpicrylhydrazyl (DPPH) was used as the reference.

In the presentation of the ESR results, $g_{\parallel}$ and $g_{\perp}$ denote the electron *g* values parallel and perpendicular to the symmetry axis of the porphyrin molecule, respectively. Correspondingly, A and B are the metal nuclear hyperfine coupling constants parallel and perpendicular to that axis. The values A_N and B_N are the observed nitrogen superhyperfine structure on the parallel and perpendicular metal resonances.

In the catalytic experiments, product distribution was followed on an F&M Model 720 gas chromatograph, with a 4 ft 10% Apiezon L on Gas Chrom S column. Conversion data were calculated relative to an internal standard, benzene.

Catalytic Experiments. A simple trickle bed reactor was made from an Liebig condensor, the jacket being connected to a circulating oil bath to provide an isothermal reaction zone. In a typical run, 10 cm^3 of 20/30 mesh resin catalyst was placed in the reactor and subjected to a mixture of dry air and of 1 *M* 1-butanethiol (BuSH) and 1 *M* benzene in hexane, both streams flowing cocurrently downward through the catalyst bed. Product liquids were collected in an ice trap and air flows were kept low (gas hourly space velocity, GHSV = 120 cm^3 of air/(cm^3 catalyst hr)) in order to avoid errors due to preferential volatilization or loss of benzene from the product. Reactor temperature was normally 25°.

Results and Discussion

Characterization of Bonded Porphyrins. Examples of covalently bonded porphyrin resins are shown in Figure 1. Of the various methods possible for bonding porphyrins to resins, only the simplest have been described and will be discussed. Included in these investigations, in addition to the amine, ester, and ketone examples, has been an alkyl (CH_2) linkage, prepared by reaction of chloromethylated TPP with XAD-2 in the presence of $AlCl_3$. The amine and ketone examples proved to be the most direct, however, and subsequent discussion will be limited to these materials and to their copper and cobalt complexes. No attempt has been made to distinguish experimentally between the singly attached, idealized structures in Figure 1 and any multiply attached or cross-linking species.

Characterization of these "polymer-attached porphyrins" proceeded initially from the following observations. (a) Polymers were treated with solutions of porphyrins according to very simple reaction sequences. When reaction was deemed complete, the polymers were extensively washed with solvent until colorless filtrates were obtained. The resins so obtained had acquired the intense purple and green colors characteristic of the porphyrin monomers. (b) Porphyrin-containing resins which were synthesized from TPP-COOH and its derivatives all exhibited carbonyl ir

Table I. Electron Spin Resonance Data of Copper Porphyrins (25°, unless noted)

Compound	$g_{\parallel}$	$g_{\perp}$	A^a	B^a	$A_N{}^a$	$B_N{}^a$	Ref
Cu[Res-NH-TPP-NH_2]	2.182	2.049	199	42	13[c]	17	*b*
Cu[Res-CO-TPP-COOH]	2.157	2.07	220	40		15	*b*
CuTPP-COOH	2.18	2.07	180	*d*	*d*	*d*	*b*
CuTPP	2.17	2.07	203	*d*	*d*	*d*	*b*
CuTPP	2.17	2.05	250	~30	*d*	*d*	28
CuTPP in $CHCl_3$	2.187	2.067	−218	−39	14.5	16.4	27

[a] In cm^{-1}, times 10^4. [b] This work. [c] At 77°K. [d] Unresolved.

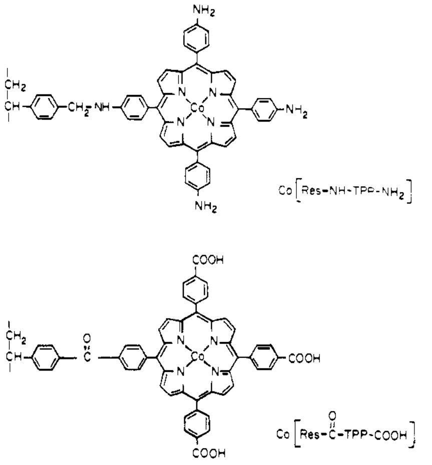

Figure 1. Cobalt complexes of polymer-bonded porphyrins.

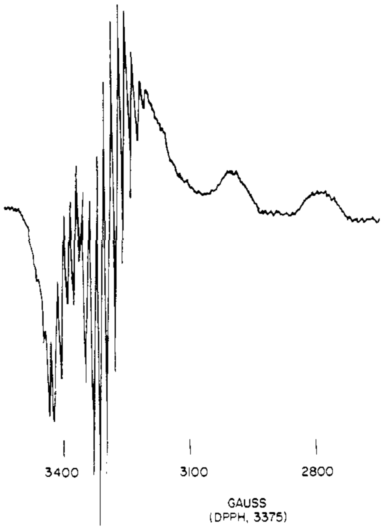

Figure 2. ESR spectrum of Cu[Res-NH-TPP-NH_2], 25°.

bands between 1670 and 1690 cm^{-1}, as detailed in the Experimental Section. (c) When treated with metal acetates, the polymers absorbed metal ion irreversibly only up to the level expected from the nitrogen content (i.e., porphyrin content).

ESR spectra of the copper derivatives provided strong and direct evidence for the presence of the porphyrins. When a Res-NH-TPP-NH_2 polymer was treated with copper acetate and thoroughly washed with 1 *N* HCl, the spectrum in Figure 2 developed. Such a spectrum is characteristic of magnetically dilute copper porphyrins and copper phthalocyanines[27] and shows clearly both nitrogen and copper hyperfine structures at room temperature. This extensive hyperfine structure suggests that the porphyrin is well dispersed within the polymer, since solid or aggregated CuTPP does not exhibit such hyperfine structure.[28] At lower temperature, additional nitrogen coupling was observed in these polymeric materials.

The spin resonance parameters are listed in Table I for a series of copper derivatives and agree well with expectations based on the literature. In Figure 2, two of the four copper resonances in the parallel orientation are observed at 2800-3100 G. Perpendicular components, with nitrogen structure, are centered about 3000, with the anomalous absorption[29] near 3400 G.

Oxidation Experiments. Thiol oxidation to disulfides is a very facile reaction in the presence of base and is rapid even at room temperature.[30,31] According to the following reaction sequence, the active species is the thiolate anion. This anion reacts with oxygen to give thiyl radicals which subsequently dimerize to the disulfide.

$$RSH + \text{base} \rightleftharpoons RS^- + H^+\cdot\text{base} \qquad (1)$$

$$2RS^- + O_2 \longrightarrow 2RS\cdot + O_2^- \qquad (2)$$

$$2RS\cdot \longrightarrow R_2S_2 \qquad (3)$$

$$O_2^- + H_2O \longrightarrow 2OH^- + 0.5O_2 \qquad (4)$$

Metal ions, particularly cobalt and cobalt complexes, promote this reaction sequence, most probably by providing an additional thiolate oxidation function according to step 5.[32] Trivalent cobalt would be regenerated by air.

$$RS^- + Co^{3+} \longrightarrow RS\cdot + Co^{2+} \qquad (5)$$

The mild nature of the thiol oxidation conditions and the known high activity of cobalt phthalocyanines and porphyrins as promoters[17,18] made this reaction an ideal choice for demonstrating the catalytic properties of polymer-bonded porphyrins. Resin polymers were tested in the trickle bed reactor with a solution of 1 *M* BuSH, 1 *M* benzene in hexane, always with a 50-100-fold excess of oxygen relative to thiol.

Table II lists the various resins tested, the cobalt content of each, and a value of 1/LHSV corresponding to a thiol conversion of 63.2%. At such a conversion level, the LHSV values would approximate the rate constants, assuming the reaction is first order. This assumption was tested (Figure 3) and found to be satisfactory.

The values of LHSV listed in Table II have been normalized to a constant cobalt loading (0.10%) and clearly identify cobalt as the oxidation center in the catalyst. Thus 63% conversion can be achieved over an amine-linked cobalt porphyrin at LHSV = 1.6. In the absence of cobalt, no conversion occurred even at considerably longer contact times (LHSV = 1.1).

In the oxidation of thiols, base has been considered the catalyst and cobalt complexes the promoters. The amine-linked cobalt porphyrin contains both functions, and it was proposed that a thiol ionization to the thiolate anion would precede oxidation. This proposal could be tested with the carboxylated porphyrin.

Resins containing covalently linked TPP-COOH can possess either acid (COOH) or base (COO^-) functions. Table II shows that, in the presence of cobalt, the carboxylate form is an effective thiol oxidation catalyst. The acid form is inactive. Neither form is active in the absence of cobalt.

Table II. Oxidation of 1-Butanethiol Over Polymer-Bonded Cobalt Porphyrins (1 *M* BuSH, 1 *M* benzene in hexane dry air GHSV = 120, 25° unless noted)

Matrix	% cobalt	1/LHSV[a]	LHSV[b]	Comments
Res-NH-TPP-NH_2	0.14	0.44	1.6	
	0.00			No reaction, LHSV 1.1
	0.14	0.42	1.7	
Res-CO-TPP-COOH	0.03			No reaction, LHSV 1.0
Na salt	0.03	2.3	1.5	
	0.03	0.92	3.6[d]	50°
	0.00			No reaction, LHSV 1.0
A-26, OH^-	0.00	0.35	(2.9)[c]	Strong base
+CoTPP-COO^-	0.10	0.13	7.7	
+TPP-COO^-	0.00	0.52	(1.9)[c]	Strong base
A-26, OH^-, H_2PTS^{4-}	0.00	0.50	(2.0)[c]	Strong base
A-26, OH^-, $CoPTS^{4-}$	0.12	0.07	11.9	

[a] 1/LHSV for 63.2% conversion of thiol, observed. [b] LHSV for 63.2% conversion, normalized to 0.10% Co. [c] Strong base catalysis, no cobalt. [d] Rapid aging.

Note, however, the similarity of the rate constants (LHSV) for the amine and carboxylate catalysts. Such a correspondence is not surprising, since the basicity of the two functional groups is similar (aniline, pK_b = 9.4; benzoic acid, pK_b = 9.8).

In ionic resins, containing both cobalt complex and excess hydroxide, oxidation proceeded rapidly. Indeed, thiol was converted even in the absence of cobalt, a result of the known strong-base catalyzed reaction path. A significant cobalt contribution to the rate was nevertheless readily apparent. In the presence of CoTPP-COO^-, conversion was achieved at LHSV = 7.7, as compared with 1.9–2.9 in the absence of the metal ion.

The rapid aging at 50° provides an indication of an undesirable side reaction. As resin catalysts experienced longer on-stream usage, a slow deactivation was observed. A portion of this deactivation could be ascribed to retention of product water by the resins and resultant hydrocarbon and thiol exclusion, particularly in the case of the hydroxide-containing resins.

It was found, however, that aged catalysts could not be regenerated by, for example, a methanol wash to remove water. Furthermore, aging was observed with a simulated refinery stream containing only 180 ppm mercaptan sulfur, a stream producing only very small amounts of water. This observation, and the failure of several attempts to regenerate spent catalysts, suggested a porphyrin or phthalocyanine decomposition even under these extremely mild reaction conditions. This suggestion is examined below.

Porphyrin Decomposition. In general, porphyrins are readily oxidized in systems containing free radicals.[33,34] The thiol reaction system would fall into this group. Indeed, several soluble porphyrins were examined for catalytic activity, including H_2TPP, VOTPP, NiTPP, CoTPP, and others. Based on spectrophotometric data, only those compounds (Co) which catalyzed the thiol oxidation were decomposed. The others were stable indefinitely.

Decomposition of the complexes CoTPP-COOH and Na_4CoPTS was followed spectrophotometrically in DMF, both at 1 × 10^{-4} *M* concentration. When BuSH was present (1 *M*), the rate of disulfide formation was simultaneously monitored.

As depicted in Table III, phthalocyanine decomposition was observed only under conditions at which thiol oxidation occurred. When no thiol oxidation took place, no catalyst decomposition was observed. Half-lives for the two catalysts, Na_4CoPTS and CoTPP-COOH, under these reaction conditions were about 150 and 40 min, respectively.

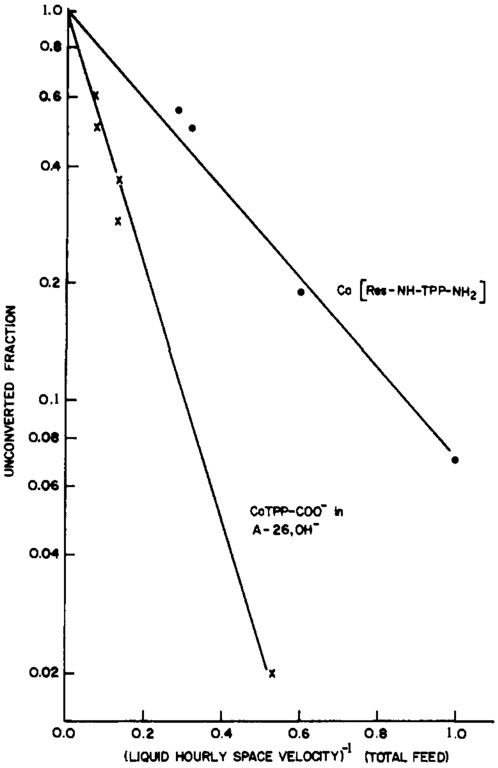

Figure 3. Oxidation of 1-butanethiol over polymer-bonded cobalt porphyrins (1 *M* BuSH, 1 *M* benzene in hexane, GHSV = 120 (air), 25°).

Table III. Factors Affecting Cobalt Phthalocyanine Decomposition (1 × 10^{-4} *M* Na_4CoPTS in DMF (1 *M* benzene, 25°))

1-BuSH[a]	NaOH[a]	Gas	Thiol oxidn	Dec
+	–	Argon	–	–
+	+	Argon	–	–
–	+	Air	–	–
+	–	Air	(–)[b]	–
+	+	Air	+	+

[a] Concentrations: BuSH, 0.9 *M*; NaOH, 1.5 × 10^{-3} *M*. [b] Trace.

The visible spectral data were in agreement with literature reports on the behavior of cobaloximes.[20] On addition of caustic, Co(II) phthalocyanine (667, 602 sh, 332 mμ) disproportionated into Co(I) and Co(III) species (708, 670, 640 sh, 605 sh, 470, 430, 320 mμ).[26,35] When BuSH was added in the absence of air or caustic, a spectrum corresponding to Co(I) resulted. In an air-saturated reaction mixture (thiol + NaOH), the predominant species was Co(III).

Conclusions

Methods have been described for the bonding of porphyrins and related ligands to porous polystyrene resins. Although only the simplest of reactions are involved, the product polymers afford an insoluble but accessible porphyrin moiety ideally suited for the study of porphyrin application to heterogeneous catalysis.

By means of various instrumental techniques, notably ir and ESR, it was shown that porphyrin integrity was maintained during attachment to the polymer. ESR spectra of the copper derivatives indicated that the porphyrin ligands were well dispersed in the resin matrix, thereby eliminating any intermolecular effects in the catalytic experiments.

Metallo and particularly cobalt porphyrins are recognized thiol oxidation catalysts,[17,18] but solubility limitations have impeded any detailed examination. It was demonstrated that thiols are cleanly oxidized to disulfides over cobalt porphyrin polymers, a reaction that is first order in unconverted thiol and, at least over a limited range, approximately first order in cobalt complex.

Effective catalysts contained both oxidation (cobalt) and proton-acceptor sites, the carboxylate form of a cobalt-TPP-COOH resin being active and the carboxylic acid form inactive. This behavior is reminiscent of a recent report of cobalt-containing poly(4-vinylpyridine) activity,[36] wherein a similar bifunctionality was contained in the catalyst.

Effective porphyrin catalysts exhibited an apparently irreversible aging, however. Those catalyst materials which were effective in the oxidation of thiols were slowly consumed or decomposed and those ineffective were quite stable. It is suggested that the free radical processes involved in thiol oxidation lead to catalyst degradation as well and that such degradation may contribute to catalyst consumption in commercial sweetening operations.[37]

The deactivation observed in this particular application should not, however, preclude potential utility in areas such as B_{12} chemistry, coordination chemistry, and porphyrin chemistry in general.

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Arene–Metal Complexes. X. Reactivity of (η^8-Benzonorbornadiene)dicarbonylchromium in the Presence of External Ligands[1]

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Abstract: Displacement of the complexed carbon–carbon double bond of (η^8-benzonorbornadiene)dicarbonylchromium (**1**) proceeds readily only in the presence of good π-acceptor ligands. This behavior is in marked contrast to that exhibited by simple (arene)(olefin)dicarbonylchromium complexes. The stability of **1** in the presence of external ligands may be attributed to the close proximity of the olefin ligand to the metal atom, i.e., a chelation effect. The complexed carbon–carbon double bond of **1** is unreactive toward various nucleophilic reagents. The spectral properties of several (η^6-benzonorbornadiene)(ligand)dicarbonylchromium complexes (**3**) indicate that increased π-bonding to the remaining carbonyl ligands accompanies the conversion of the corresponding tricarbonyl complex to **3**. This is reflected in the behavior of complexes with structure **3** upon photolysis since in all cases the ligand is removed in preference to a carbonyl group.

An interesting new class of compounds, (alkenylarene)dicarbonylchromium complexes, has recently been formulated in our laboratory.[2] In these complexes the organic ligand contains both a benzene nucleus and a carbon–carbon double bond, and both of these groups are bonded to the metal to occupy four metal coordination sites. Since compounds of this kind might be expected to exhibit properties unlike those of simple olefin complexes,[3,4] an investigation of the reactivity of (η^8-benzonorbornadiene)dicarbonylchromium (**1**) was initiated.

Results

Complex **1**, a red crystalline solid, is readily available from photolysis (>300 nm) of (η^6-benzonorbornadiene)tri-