dimer units would be coupled only through the bridging iodide ligands and Mo–Mo interactions between the two coupled dimers would be negligible.

Some insight into the structure of β-$MoCl_2$ may be provided by the formation of this material by loss of ligands from $Mo_4Cl_8L_4$ (L = MeOH, THF). Previous workers[15] postulated that amorphous to poorly crystalline β-$MoCl_2$ contained quadruply bonded dimeric units because (1) the material is usually prepared by reaction of $Mo_2(O_2CCH_3)_4$ with gaseous HCl and (2) the dimeric complexes $Mo_2Cl_4(PR_3)_4$ are obtained upon reaction of β-$MoCl_2$ with excess trialkylphosphine reagent. However, the work reported here establishes that β-$MoCl_2$ may be formed from the tetrameric $Mo_4Cl_8L_4$ clusters under very mild conditions, especially when L = THF, and that the tetrameric clusters also provide $Mo_2Cl_8(PR_3)_4$ dimers upon reaction with excess trialkylphosphine. Thus the new evidence indicates that β-$MoCl_2$ may consist of rectangular tetrameric units rather than dimeric units. Work designed to elucidate the structural features and chemical properties of β-$MoCl_2$ is being continued in this laboratory.

Acknowledgment. We thank the National Science Foundation for a grant to the Department of Chemistry for the purchase of the photoelectron spectrometer used in this research.

Registry No. $Mo_4Cl_8(CH_3OH)_4$, 78165-72-7; $Mo_4Cl_8(CH_3CH_2CN)_4$, 78264-81-0; $Mo_4Cl_8(C_4H_8O)_4$, 80822-42-0; $Mo_4Cl_8[P(C_6H_5)_3]_4$, 80822-43-1; $Mo_2Cl_2(O_2CCH_3)_2[P(C_6H_5)_3]_2$, 80822-44-2; $Mo_4Cl_8(PEt_3)_4$, 68568-88-7; $Mo_4Cl_8[P(n\text{-}C_4H_9)_3]_4$, 68568-89-8; $Mo_2Cl_4[P(n\text{-}C_4H_9)_3]_4$, 38832-72-3; $Mo_4Br_8[P(n\text{-}C_4H_9)_3]_4$, 80822-45-3; $Mo_4I_8[P(n\text{-}C_4H_9)_3]_4$, 80822-46-4; $Mo_2Cl_4[P(C_6H_5)_3]_2(CH_3OH)_2$, 68569-21-1; $\{MoCl_2[P(C_6H_5)_3]\}_n$, 80822-56-6; $Mo_2I_4(P\text{-}n\text{-}Bu_3)_4$, 80822-38-4; $(NH_4)_4Mo_2(SO_4)_4\cdot 2H_2O$, 80822-47-5; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $(NH_4)_5Mo_2Cl_9$, 61583-95-7; $K_4Mo_2Cl_8$, 25448-39-9; $(NH_4)_4Mo_2Br_8$, 61520-69-2; $Mo(CO)_6$, 13939-06-5; $(CH_3)_3SiCl$, 75-77-4; $(CH_3)_3SiBr$, 2857-97-8; $(CH_3)_3SiI$, 16029-98-4; $AlCl_3$, 7446-70-0.

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Monomeric Polymer-Anchored Molybdenum(V) Coordination Complexes

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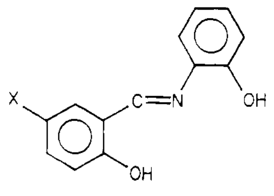
The synthesis and EPR characterization of monomeric, polymer-anchored Mo(V) coordination complexes are described. Tridentate Schiff base ligands derived from 5-X-salicylaldehyde (X = H, NO_2) and 4-amino-3-hydroxybenzoic acid were employed. The Schiff base ligand is covalently attached as an ester through the carboxylic acid function of the ligand to a polystyrene matrix. The polymer-anchored ligand has the same structure and coordination geometry as the analogous free ligand, *N*-(5-H-salicylidene)-2-aminophenol (5-H-SAP-H_2), whose monomeric Mo(V) complex has already been described. $(NH_4)_2MoOCl_5$ is the source of Mo(V) used for the synthesis of the monomeric polymer-anchored Mo(V) coordination complexes. The polymer-anchored Mo(V) complexes are stabilized as monomers for as long as 1 month as is evidenced by no decrease in the intensity of the EPR signal. The anisotropic EPR spectrum and parameters for the polymer-anchored [P]-5-H-SAP-Mo^VOCl (where [P] = polymer-anchored complex) is essentially identical with that observed for the free complex $(Et_4N)MoO(5\text{-H-SAP})Cl_2$. The EPR results indicate that the electronic structure and stereochemistry of [P]-5-H-SAP-Mo^VOCl are unchanged from those of the well-characterized $(Et_4N)MoO(5\text{-H-SAP})Cl_2$. In DMF, the polymer-anchored Mo(V) complexes are oxidized by NO_3^- with complete loss of the Mo(V) EPR signal.

Introduction

The coordination chemistry of molybdenum has been the subject of intensive study in recent years because of its importance in numerous biochemical redox reactions associated with such enzymes as xanthine oxidase, nitrate reductase, and nitrogenase among others.[1] It is well established that molybdenum is a necessary cofactor for these enzymes.[2] During catalysis, the Mo(V) oxidation state has been identified by electron paramagnetic resonance (EPR) spectroscopy for xanthine oxidase, sulfite oxidase, aldehyde oxidase, and nitrate reductase.[1-3] The EPR signal appears to arise from a monomeric Mo(V) center as a result of electron transfer to or from the substrate. Recent EXAFS studies have established the presence of terminal molybdenum–oxo groups in the oxidized forms of xanthine oxidase[4] and sulfite oxidase.[5] It is also known that in those enzymes that catalyze oxidation reactions, water is the oxygen atom source.

In a previous report,[6] it was shown that stable *cis*-dioxomolybdenum(VI) coordination complexes can be prepared with the tridentate Schiff base ligand 5-X-SAP-H_2 (X = H, Br, NO_2, CH_3O). The cathodic reduction potentials (E_{p_c}) for the Mo(VI) complexes spanned a range of ~200 mV on going from X = NO_2 to X = CH_3O. A linear relationship was observed between E_{p_c} and the Hammet σ_p parameter for the X substituent on the ligand. A logical extension of this work would involve the synthesis and characterization of analogous Mo(V) coordination complexes.



5-X-SAP-H_2 (X = H, **1a**; X = NO_2, **1b**)

In contrast to the molybdenum enzymes, the aqueous chemistry of simple Mo(V) complexes is dominated by EPR silent oxo- or sulfido-bridged dimers.[1] Recently, it has been shown that monomeric Mo(V) complexes can be obtained in solution but only under experimental conditions that rigorously excluded H_2O.[7-10] Spence and co-workers have described the

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electrochemistry,[7] EPR spectroscopy,[10] and reactivity with NO_3^-[9] of the monomeric Mo(V) complex obtained with the 5-H-SAP^{2-} ligand. This complex is sensitive to traces of H_2O in the solvent. Their work showed that the monomeric Mo(V) complex dimerized upon standing even in dry DMF. Significant dimerization occurred within 24 h.

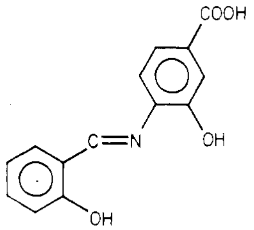
With the Mo(V) complexes covalently anchored to rigid, insoluble polymer supports, the possibility exists for isolating reactive Mo(V) centers apart from each other thereby blocking dimer formation. Polymer-anchored transition-metal complexes have been studied in recent years especially in the area of noble-metal catalysts.[11] There has also been work in this area with regard to bioinorganic model systems. Garner and co-workers have reported on the reduction of MoO_2(ethyl L-cysteinate)$_2$ mixed in a polystyrene suspension.[12] In other work, Mitchell and Taylor described Mo(V) complexes with a polykis(iminoethylene)dithiocarbamate copolymer.[13] Suzuki et al. have prepared a dextran-bound binuclear molybdenum(V) cysteine complex[14] while Huche and co-workers have prepared a polymer-anchored molybdenum(VI) cysteine complex.[15] Both cysteine systems are reported to reduce acetylene in the presence of $NaBH_4$. Topich has described the synthesis and reactions of polymer-anchored Mo(V) and Mo(VI) tripeptide complexes.[16] One difficulty that arises with many of these studies concerns itself with the detailed characterization of the polymer-anchored species.

This paper describes the synthesis and EPR characterization of polymer-anchored Mo(V) complexes which incorporate the tridentate Schiff base ligands 5-H-SAP-H_2 and 5-NO_2-SAP-H_2.

Results and Discussion

The major difficulty that arises in working with transition-metal complexes that are covalently anchored to insoluble polymer supports results from the fact that most normal methods of characterization (UV–visible, IR, and NMR spectroscopy, elemental analysis, etc.) do not yield useful results. To overcome this problem of characterization, it was necessary to develop an experimental strategy whereby a simple, nonanchored, well-characterized, monomeric Mo(V) complex would serve as the prototype metal complex. Then an essentially identical complex would be covalently attached to the polymer support. It is reasonable to assume that if the coordination sphere about the metal is not changed in going from the free to the polymer-anchored metal complex, then the characterization results obtained for the free complex are directly applicable to the polymer bound complex as well. For synthetic utility, the organic ligand is first coupled to the polymer and then the Mo(V) complex is synthesized. So that the goal of preventing Mo(V) dimer formation on the polymer could be accomplished, several important requirements must be met. Some relate to the polymer support itself while others involve the nature of the ligand. Polystyrene, 1% cross-linked with divinylbenzene, was chosen because it gives a polymer support which is both rigid and insoluble in most common organic solvents. The polystyrene must then be chemically modified to provide a reactive site for ligand attachment. The polystyrene used in this work was chloromethylated to the degree of 0.001 mol of Cl/g of polymer. A rough calculation shows that this amount of Cl means that the chloromethylation took place on phenyl rings that are eight to ten styrene units apart as one goes along the polymer chain. The ligand is attached by nucleophilic displacement of the Cl. In order to insure that monomeric Mo(V) complexes and not dimers are attached to the polymer it is useful if the entire ligand is comprised of just one unit and that there be no free ligand in solution when the Mo(V) salt is added. If free ligand is present in solution, there is a high probability of anchored and free Mo(V) dimers being formed.

The prototype complex which is to serve as the model for the polymer-anchored Mo(V) complex is $[Mo^VO(5\text{-H-SAP})Cl_2]^-$, which has been described in the literature.[7,9,10] An examination of the ligand (**1a**) shows that the coordination sphere about the Mo would be altered if the ligand were attached to the polymer as an ether through either of the two phenolic oxygens. Although this is a potential mode of attachment for the ligand, it is not preferable because then a direct comparison of the polymer-anchored Mo complex with the well-characterized free complex is no longer possible. So that this unwanted situation could be avoided, the ligand which is attached to the polymer is a slightly modified version of 5-X-SAP-H_2. Instead of reacting salicylaldehyde with *o*-aminophenol, salicylaldehyde is reacted with 4-amino-3-hydroxybenzoic acid to yield a ligand with the following structure:



A comparison of this ligand with 5-H-SAP-H_2 shows that the tridentate ONO coordination sphere is maintained with the only difference being the external carboxylic acid function. This group is included as a part of the ligand in order to serve as the site for coupling of the ligand to the chloromethylpolystyrene. Merrifield[17] has described a procedure for the coupling of amino acids to chloromethylpolystyrene. The amino acids are coupled to the polymer as esters through the carboxylic acid group. A similar coupling procedure was followed here. Although the possibility exists for the ligand to couple to the polymer as an ether through either of the phenolic oxygens, the EPR results to be presented later for the Mo(V) polymer-anchored complex indicate that the ONO coordination sphere has not been disturbed and coupling has in fact taken place through the carboxylic acid group. The ligands are orange while the chloromethylpolystyrene is white. After the ligand–polymer coupling reaction is complete, the polymer support takes on the orange color of the ligand and this color remains on the polymer even after exhaustive washings. The polymer-anchored ligand or its triethylammonium salt can then be used for the synthesis of the appropriate transition metal complexes. $(NH_4)_2MoOCl_5$ is used as the source of Mo(V). The synthesis of the polymer-anchored Mo(V) complex is carried out in dry DMF since this solvent causes considerable swelling of the polymer beads. Immediately after the filtered DMF solution of the Mo(V) salt is added to the DMF slurry of the polymer-anchored ligand, the polymer beads change from orange to brown as the complex is formed. It is worthy to note that the free $[Mo^VO(5\text{-H-SAP})Cl_2]^-$ is also a brown solid. The brown color cannot be rinsed off the polymer during exhaustive washings

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Table I. EPR Parameters

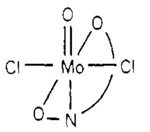
	$g_\parallel$	$g_\perp$	$A_\parallel^{Mo}$, G	$A_\perp^{Mo}$, G	ref
[P]-5-H-SAP-Mo^VOCl	1.929[a]	1.947[a]	80.7[b]	36.2[b]	*c*
[P]-5-NO_2-SAP-Mo^VOCl	1.960	1.942	76.5	*d*	*c*
$(Et_4N)MoO(5\text{-}H\text{-}SAP)Cl_2$	1.923	1.947	82.6	36.8	10

[a] ±0.005. [b] ±1.25 G. [c] This work. [d] Obscured.

with DMF or dichloromethane. Although the color changes observed on the polymer surface hint that the desired polymer-anchored Mo(V) complex has been formed, a more precise method of characterization is necessary. Many common methods of chemical characterization do not yield useful results because of the polymer-anchored nature of the Mo(V) complex. EPR spectroscopy, however, is a technique that can be used to probe the nature of this complex.

The principal reason for covalently attaching Mo(V) complexes to insoluble polymer supports is to stabilize monomeric Mo(V) complexes by physically preventing dimer formation via the rigid polymer backbone. It is essential in this study to quantify the amount of monomeric Mo(V) complex covalently linked to the polymer support. For several samples the average amount of Mo attached to the polymer is $(5.5 \pm 0.5) \times 10^{-5}$ mol of Mo/g of polymer as determined by elemental analysis (atomic absorption spectroscopy). Quantitative EPR measurements show that the amount of monomeric Mo(V) present is 60 ± 10% of the total Mo present on the polymer. This is a significant amount of monomeric Mo(V) since one cannot expect all of the polymer-anchored ligands to be physically separated from each other. The polymer is crosslinked, having polymer chains twisted and overlapped which must bring some of the reactive groups near one another. A point which is important to recognize concerns the synthesis of the polymer-anchored Mo(V) complex. This synthesis involves the polymer-anchored ligand and the Mo(V) salt being in solution for 24 h. If the Mo(V) complexes formed were not polymer-supported, there would have been significant dimerization during the 24 h as is discussed by Taylor et al.[7] These results show convincingly that the polymer-anchored Mo(V) complex can be stabilized for long periods of time under conditions where free monomeric complexes would dimerize.

Chasteen and co-workers[10] have described a detailed EPR study of $(NH_4)_2MoOCl_5$ and a series of its derivatives which include bi-, tri- and tetradentate ligands. Of interest is the EPR results for the Mo(V) complex of 5-H-SAP^{2-}. $(Et_4N)MoO(5\text{-}H\text{-}SAP)Cl_2$ has been shown to have the following stereochemistry:[10]



In DMF, $MoO(5\text{-}H\text{-}SAP)(CH_3OH)Cl$ and $(Et_4N)MoO(5\text{-}H\text{-}SAP)Cl_2$ have electronic and EPR spectra and cyclic voltammograms which are identical.[9] It is therefore reasonable to assume similar structures for these two complexes and that in DMF, CH_3OH or Cl^- is probably easily replaced by the solvent. The EPR parameters for this complex are listed in Table I. The EPR results reported by Chasteen and co-workers[10] were obtained by computer simulation of the experimental spectra both at X- and Q-band frequencies.

Figure 1 shows the room-temperature EPR spectrum for the polymer-anchored MoO(5-H-SAP)Cl complex. Abbreviations to be used for the polymer-anchored Mo(V) complexes are [P]-5-X-SAP-Mo^VOCl (X = H, NO_2). The spectrum that is observed is an anisotropic spectrum even at room temperature because the Mo(V) complex is covalently attached to the rigid polymer support. The solid, insoluble polymer beads are packed in a conventional EPR sample tube, and the spectrum is obtained under normal instrument conditions. The spectrum is easily analyzed because of the distribution of the naturally occurring isotopes of molybdenum. The EPR spectrum is unchanged at −130 °C. The unique result which is obtained from the EPR spectrum of the polymer-anchored Mo(V) complex described here is that the spectral shape as well as the *g* and *A* parameters are, within experimental error, identical with those of the frozen glass spectrum and parameters presented by Chasteen and co-workers for $(Et_4N)MoO(5\text{-}H\text{-}SAP)Cl_2$.[10] In their report, they described EPR results for ten Mo(V) complexes and there are substantial differences between them. This indicates that the EPR results can be used as an identification tool. The remarkable similarity between the EPR spectra of [P]-5-H-SAP-Mo^VOCl and $(Et_4N)MoO(5\text{-}H\text{-}SAP)Cl_2$ serves as very convincing evidence as to the nature of the polymer-anchored Mo(V) complex. The EPR results show that the Mo(V) complex has been successfully anchored to the polymer support and that the stereochemistry and electronic structure of the polymer-anchored complex is identical with that of the free Mo(V) complex that has been described in the literature.

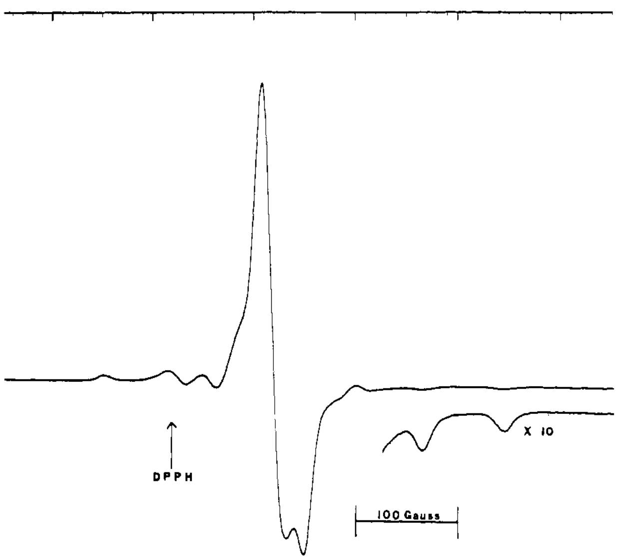


Figure 1. Room-temperature EPR spectrum of [P]-5-H-SAP-Mo^VOCl. Microwave frequency is 9.548 GHz.

EPR spectra for [P]-5-X-SAP-Mo^VOCl (X = H, NO_2) were recorded every few days for 1 month. The EPR sample tubes were filled under a nitrogen atmosphere and then stoppered with septa caps. No additional precautions were taken in handling the EPR samples during the month of observation. The spectra showed no significant loss of intensity over this period. This result indicates that one of the major objectives of this work has been achieved in that Mo(V) monomers can be stabilized for long periods by covalently linking the complex to a rigid polymer support.

So that it could be seen if small changes in the ligand structure would affect the observed EPR parameters, the Schiff base ligand derived from the condensation of 5-nitrosalicylaldehyde and 4-amino-3-hydroxybenzoic acid was also prepared. This ligand is the carboxylic acid analogue of **1b**. The attachment of the ligand to the polymer and the synthesis of the Mo(V) complex was accomplished as described above. The EPR spectrum for this complex is shown in Figure 2. EPR parameters are listed in Table I. An examination of this EPR spectrum shows significant differences when compared to the spectrum obtained for [P]-5-H-SAP-Mo^VOCl. The first major difference is that $g_\parallel > g_\perp$ and $g_\parallel$ (X = NO_2) > $g_\parallel$ (X = H). In addition $A_\parallel^{Mo}$ for [P]-5-NO_2-SAP-Mo^VOCl is smaller than $A_\parallel^{Mo}$ for [P]-5-H-SAP-Mo^VOCl by approximately 4–5 G. The

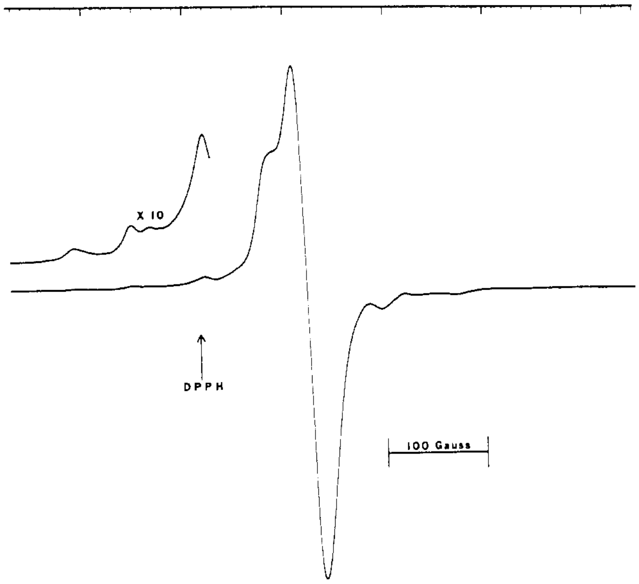


Figure 2. Room-temperature EPR spectrum of [P]-5-NO_2-SAP-Mo^VOCl. Microwave frequency is 9.548 GHz.

smaller value of $A_\parallel^{Mo}$ for [P]-5-NO_2-SAP-Mo^VOCl is expected in light of some electrochemical experiments on some similar *cis*-dioxomolybdenum(VI) coordination complexes.[6,18] The 5-NO_2-SAP^{2-} ligand was shown to be more electronegative when compared to 5-H-SAP^{2-}. Although the NO_2 group is not directly coordinated to the molybdenum, its electron-withdrawing effect is transmitted to the metal through the delocalized ligand system. The 5-NO_2-SAP^{2-} ligand effectively draws electron density away from the molybdenum and this is manifested in the smaller value of $A_\parallel^{Mo}$ when compared to [P]-5-H-SAP-Mo^VOCl. The low symmetry of these polymer-anchored Mo(V) complexes makes it difficult to draw any theoretical conclusions concerning excited-state contributions which effect the magnitudes of $g_\parallel$ and $g_\perp$.

In DMF, the polymer-anchored Mo(V) complexes are oxidized by NO_3^- in a manner similar to that described by Spence and co-workers[9] for some simple Mo(V) complexes. During the reaction, the Mo(V) EPR signal is lost and NO_2^- is detected by the method of Shinn.[19] Since the EPR results have shown that the free and polymer-anchored Mo(V) complexes are very similar it is reasonable to assume that NO_2 is produced during the reaction. This is the product identified by Spence et al. for the reaction of the free Mo(V) complex with NO_3^-. The NO_2 then disproportionates into NO_2^- and NO_3^- under the conditions for the colorimetric determination of NO_2^-.

The results described here have shown that it is feasible to take a simple Mo(V) coordination complex, make a minor modification of the ligand backbone, and attach this complex to an insoluble polymer support. The EPR results show unambiguously that the stereochemistry and electronic structure of the polymer-anchored Mo(V) complex is essentially identical with those of its free Mo(V) analogue. The most important result that has come out of this work is the fact that the polymer-anchored monomeric Mo(V) complex is stabilized for long periods because the pathway for Mo(V) dimer formation is blocked. Finally, the polymer-anchored Mo(V) complexes are oxidized by NO_3^- with complete loss of the Mo(V) EPR signal.

Experimental Section

Materials. Salicylaldehyde, 5-nitrosalicylaldehyde, and 4-amino-3-hydroxybenzoic acid were obtained from commercial sources and used without further purification. Chloromethylated polystyrene (0.001 mol Cl/g; 1% cross-linked) was purchased from the Sigma Chemical Co. under the name of Merrifield's Peptide Resin. $(NH_4)_2MoOCl_5$ was synthesized according to the procedure of Winkler.[20] *N,N*-Dimethylformamide (DMF), anhydrous ethyl acetate, and absolute ethanol were reagent grade. DMF was dried over type 3A molecular sieves.

Synthesis. The ligands were obtained via a Schiff base condensation reaction between either salicylaldehyde or 5-nitrosalicylaldehyde and 4-amino-3-hydroxybenzoic acid. The reactions were run in absolute ethanol. The ligands are orange crystalline solids, and they were characterized by IR and NMR spectroscopy.

Polymer-Anchored Ligands. The coupling of the ligand to the polymer was carried out as follows. The ligand (0.012 mol) was dissolved in 30 mL of DMF. To this solution was added 4 g of the white chloromethylated polystyrene beads. This mixture was stirred for 10 min at room temperature to allow for the swelling of the polymer beads. The polymer beads are insoluble in the solvents used here. At this point, 100 mL of anhydrous ethyl acetate and triethylamine (0.014 mol) were added to the mixture. This mixture was then brought to gentle reflux for 4 h. The suspension was then filtered, and the polymer beads were exhaustively washed with DMF and ethyl acetate. After being washed, the polymer beads were air dried. The polymer beads take on the orange color of the covalently attached ligand.

Polymer-Anchored Mo(V) Complexes. The synthesis of the polymer-anchored Mo(V) complexes was carried out under a nitrogen atmosphere in a Vacuum Atmospheres dry box. The polymer-anchored ligand (1 g) was suspended in 75 mL of DMF. This suspension was stirred for 10 min to allow the polymer beads to swell. An excess of $(NH_4)_2MoOCl_5$ (0.002 mol) was dissolved in 25 mL of DMF, and this solution was filtered and then added with stirring to the polymer-anchored ligand suspension. The color of the polymer beads immediately changed from orange to brown. The mixture was stirred for 24 h, filtered, and then exhaustively washed with DMF. The polymer beads containing the covalently-anchored Mo(V) complex were then dried under vacuum and stored in the drybox.

Physical Measurements. The EPR spectra were recorded with a Varian E-9 spectrometer equipped with a Varian E4540 variable-temperature unit. All EPR spectra were calibrated with DPPH. The amount of EPR-active Mo(V) on the polymer was determined by double integration of the room-temperature EPR spectra with the use of a toluene solution of DPPH as a spin concentration standard. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Acknowledgment. Support of this research by the Research Corp. and by the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, is gratefully acknowledged.

Registry No. 3-Hydroxy-4-[[(2-hydroxyphenyl)methylene]amino]benzoic acid, 53899-51-7; 3-hydroxy-4-[[(2-hydroxy-5-nitrophenyl)methylene]amino]benzoic acid, 80664-92-2; $(NH_4)_2MoOCl_5$, 17927-44-5; polystyrene, 9003-53-6; salicylaldehyde, 90-02-8; 5-nitrosalicylaldehyde, 97-51-8; 4-amino-3-hydroxybenzoic acid, 2374-03-0.

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