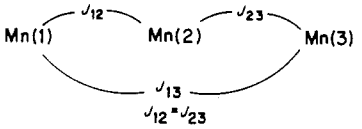
magnetic moment at 300 K is 4.97 μ_B in agreement with the spin-only value (4.90 μ_B). A sharp decrease in the moment below approximately 15 K is indicative of zero field splitting, and a value of 5.71 cm^{-1} has been obtained by least-squares fitting of the data. Dimers **1**, **3**, and **4** all possess moments per Mn at 300 K (4.51, 3.95, and 3.97 μ_B, respectively) that are below spin-only values and that decrease to near-zero values with decreasing temperature. Antiferromagnetic coupling of two high-spin d^4 Mn(III) centers to yield singlet ground states is thus indicated, and satisfactory least-squares fits to the data have been obtained, assuming an isotropic exchange interaction with a spin Hamiltonian $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ and $S_1 = S_2 = 2$. Values of the exchange parameter J are -1.9, -18.7, and -18.7 cm^{-1}, respectively. The behaviors of **3** and **4** are thus very similar, as expected from their similar structures; the slight difference in their Mn··Mn distances is obviously not reflected to a noticeable degree in their magnetic properties.

Trimer **5** has a moment of 6.75 μ_B at 300 K decreasing to ~3.9 μ_B below ~25 K, corresponding to a spin quartet ($S = {}^3/_2$) ground state. The data were fit to the magnetic susceptibility equation derived with two exchange parameters, defined by



Satisfactory fits have been obtained, however, by taking $J_{13} = 0$ with $S_1 = S_3 = 2$ and $S_2 = {}^5/_2$, yielding a value of $J_{12} = J_{23} = -18.3$ cm^{-1}. Allowing J_{13} to vary leads to only very small values of this parameter, and has an almost insignificant effect on the quality of the fit or the value of J_{12}.

The combined magnetic data thus demonstrate that complexes **1**-**5** all contain high-spin metal centers, which, with the exception of Mn(2) in **5**, are in the +3 oxidation level. In addition, **1**, **3**, **4**, and **5** are antiferromagnetically coupled with values of the exchange parameter J that are relatively small ($|J| < 20$ cm^{-1}).

The results described above serve to further emphasize the accessibility and stability of the Mn(III) oxidation level in a thiolate environment. The usual redox instability of Mn(III) to readily oxidizable thiolate functions is suppressed by use of dithiolate ligands. One important aspect of **5** in this respect has been to demonstrate that the stabilization of Mn(III) is not due to some unique property of the edt^{2-} ligand. Armed with this reassurance, conditions are now being sought to stabilize Mn(III) with other thiolates, including monothiolates, and with additional biologically relevant ligands.

Acknowledgment. This research was supported by Research Corp., by the donors of the Petroleum Research Fund, administered by the American Chemical Society, by BRSG Grant SO7 RR07031 awarded by the Biomedical Research Support Grant Program of the National Institutes of Health, and by National Institutes of Health Grant HL 13652 (D.N.H.). We thank the Bloomington Academic Computing Service for a gift of computer time.

Supplementary Material Available: Listings of fractional atomic coordinates and isotropic thermal parameters for non-hydrogen atoms (4 pages). Ordering information is given on any current masthead page.

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Received April 29, 1985

Polymer-Pendant Ligand Chemistry. 1. Reactions of Organoarsonic Acids and Arsenic Acid with Catechol Ligands Bonded to Polystyrene-Divinylbenzene and Regeneration of the Ligand Site by a Simple Hydrolysis Procedure

Sir:

The use of polymer-supported pendant ligands for metal ion removal is a well-developed field.[1] More recent studies have focused on specific reactions of these polymer-bonded ligands and include separations of biological substrates,[2a] protein fractionation,[2b] racemate separations,[2c] and transport of cations through membranes.[2d] Interestingly, very few of the reported methods incorporate a chemical reaction that forms discrete covalent metal-heteroatom bonds with loss of a small molecule such as water for the metal ion removal step; but rather, they usually entail an ion exchange or binding phenomena for reaction to occur.[3]

Additionally, an important area concerning processing of complex matrices such as synthetic fuels and petroleum crudes, for the removal and recovery of trace organometallic compound contaminants, has received little or no attention in this field[4] due to the lack of molecular characterization of these carbon-metal-bonded compounds in these sources. Thus, it is evident from an environmental and economic standpoint, that new and innovative methods for removal and recovery of trace organometallic compounds as well as inorganic anions from the above-mentioned matrices would be useful.

In this communication, we wish to report a novel method for reactions of organoarsonic acids and arsenic acid, known to be present in oil shale and its pyrolysis products,[5] with catechol ligands bonded to either 2% or 20% cross-linked methylated polystyrene-divinylbenzene (PS-DVB) resins.[6] A previous study with catechol-bonded ligands on PS-DVB resins dealt with their reactions with metal ions in aqueous solution and showed a selectivity toward Hg^{2+} ions.[7] As far as we have been able to determine, reactions of this polymer-supported ligand with organometallic compounds or inorganic anions have not been reported.

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(6) Synthesized by reaction of catechol with 2% or 20% chloromethylated polystyrene-divinylbenzene resins in the presence of stannic chloride to provide an 11% by weight (2%) and 6% by weight (20%) incorporation of catechol in the polymer. See: Warshawsky, A.; Kahana, N. *J. Am. Chem. Soc.* **1982**, *104*, 2663.

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Table I. Removal of Arsenic Compounds **1–3** from Solution Using both 2% and 20% Cross-Linked Catechol-Bonded PS-DVB Resins[a]

	2%[b,c]		20%[b,c]	
arsenic compd	concn, mmol of As/g	% removed	concn, mmol of As/g	% removed
1	0.503[d]	100	0.232	86
2	0.307	62	0.20	74
3	0.212	64	0.124	69

[a] A 100-mg sample of catechol-bonded resin, 2% or 20% cross-linked, containing 1.0 mmol/g, 11% by weight, of catechol or 0.538 mmol/g, 5.92% by weight, of catechol, respectively. [b] Reaction conditions for compounds **1** and **2**: initial arsenic to catechol concentration is 1:2 at 80 °C for 18 h in benzene (10 mL) under nitrogen. [c] Reaction conditions for compound **3**: initial arsenic to catechol concentration is 1:3, 81 °C, 17 h, 90% ethanol (10 mL) under nitrogen. [d] After reaction, the beads were filtered and washed well with hot methanol, quartz-distilled water and again with methanol. The washings were added to the filtered solution and analyzed for arsenic by single-cup graphite furnace atomic absorption spectrometry.

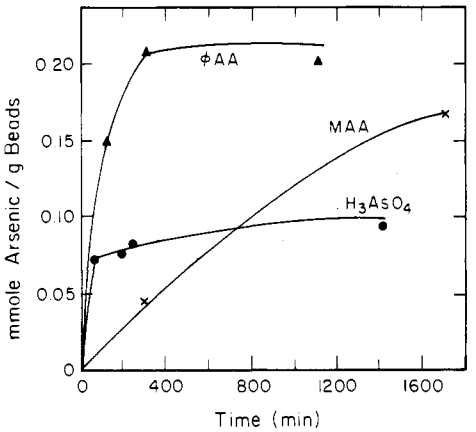

Figure 1. Rates of removal of ϕAA (**1**), MAA (**2**), and H_3AsO_4 (**3**) from solution with 20% cross-linked catechol-bonded resin (5.92% catechol by weight). See Table I for reaction conditions for compounds **1–3**.

The bonded catechol ligands were reacted with phenylarsonic acid (**1**) and methylarsonic acid (**2**) in benzene or with arsenic acid (**3**) in 90% aqueous ethanol to provide the corresponding polymer-bonded 1:2 (**1** and **2**, eq 1) or 1:3 (**3**) arsenic catecholates.[8]

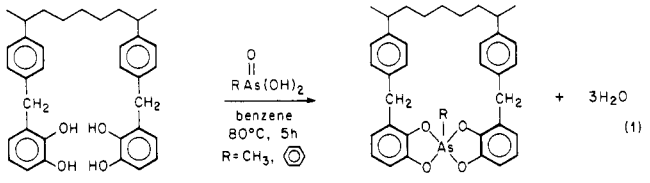

Table I provides the concentrations (mmol of As/g of resin) of **1–3** removed from solution, while the 2% cross-linked resin is compared to the 20% analogue. In addition, the rates of removal from solution of compounds **1–3** can be shown graphically by plotting mmol of arsenic/g of resin (20%) vs. time, and this is illustrated in Figure 1. From the results in Table I and Figure 1, compound removal values are **1** > **2** > **3** for the 20% cross-linked resin, while the initial rate ratio for **1**/**2** is ~7.3. This latter initial rate ratio for **1** and **2** could not be readily compared to **3**, because of solvent and molar ratio differences in their respective reactions, i.e. benzene for **1** and **2** and aqueous ethanol for **3** and arsenic to catechol ratios of 1:2 and 1:3, respectively. Furthermore, we verified the 1:2 and 1:3 ratios of arsenic to catechol for **1**, **2**, and **3**, respectively, by varying the ratio of the two reactants and finding the maximum percentages removed at the above-mentioned stoichiometries. The greater reactivity of **1** over **2** toward the polymer-bonded catechol ligand is probably a consequence of the stronger acidity of **1** to **2**, while the proximity of catechol groups in the polymer may affect total reaction conversion (e.g., compound **3**).

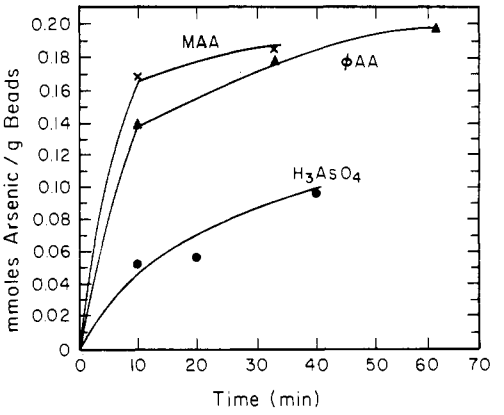

Figure 2. Rates of hydrolysis (Na_2CO_3, 1 h, 63% aqueous ethanol, 65 °C) of the bonded arsenic catecholates to provide ϕAA (**1**), MAA (**2**), H_3AsO_4 (**3**) (20% cross-linked resin). Initial arsenic concentration on the resin: **1**, 0.232 mmol of As/g; **2**, 0.2 mmol of As/g; **3**, 0.124 mmol of As/g.

We attempted to verify structures of the polymer-bonded arsenic catecholates by comparing the infrared spectrum (KBr) of the polymer-supported catechol resin with those of the resins containing compounds **1–3** after reaction with the bonded catechol ligands. Unfortunately, IR bands due to As–O stretching frequencies, ~680–700 cm^{-1}, were masked by PS-DVB aromatic C–H deformations as well as by those of the catechol ligands. However, we did see dramatic changes in the IR spectra of the bonded arsenic catecholates. For example, IR bands at 1250, 1115, and 870 cm^{-1}, attributed to the OH deformations of the bonded catechol ligands, were not apparent in the IR spectra of the bonded arsenic catecholates. We feel that this IR result qualitatively substantiates reactions of **1**, **2**, and **3** with the bonded catechols.

It is also apparent from Table I that the 2% cross-linked swellable resins contain the higher concentration of catechol and consequently can remove almost twice the concentration of arsenic compounds, **1–3**, from solution. However, for this application, we found the macroreticular 20% cross-linked resins easier to handle in filtrations and constant reuse; thus we preferred to use these resins in both removal and regeneration experiments.

In this regard, the ligand site could be easily regenerated by a simple hydrolysis procedure using a solution of sodium carbonate (6.3×10^{-2} M) in either 63% aqueous ethanol or quartz-distilled water at 65 °C for 1 h. Figure 2 demonstrates the rapid ligand regeneration reaction for the 20% cross-linked resins containing the arsenic catecholates. Importantly, from 40 to 85% of arsenic compounds **1–3** are recovered after approximately the first 10 min of hydrolysis with rates of hydrolysis being **2** > **1** > **3**. Further arsenic compound hydrolysis is provided after 1 h (5–10%) by reaction with a sodium bicarbonate solution (7×10^{-2} M, 1 h, 65 °C), which also regenerates the catechol site for reuse. It is then important for continued reuse to wash the catechol-bonded resins with hot water and methanol to remove carbonates and finally to dry the resin under vacuum (95 °C, 1 h) to remove water. The above mentioned removal (uptake) and hydrolysis procedures were repeated at least three times for compounds **1–3** with consistent results (Table I).

Clearly, these polymer–pendant ligand reactions with organometallic and inorganic compounds have the potential of being highly useful in either synthetic purification procedures or in processing applications.[9] We are continuing our studies on polymer–pendant ligand chemistry directed toward organometallic and inorganic compound removal from synthetic fuels and pe-

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troleums using appropriate compounds characterized in the above-mentioned matrices as well as testing other bonded ligands.

Acknowledgment. We wish to thank Dr. Abraham Warshawsky of the Weizmann Institute for reprints and a review of the selective ion exchange polymer field. This study was supported by the Assistant Secretary of Fossil Energy and Division of Oil, Gas and Shale Technology and the Bartlesville Project Office of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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Received June 5, 1985

A Cytochrome b_5 from Erythrocytes of *Phascolopsis gouldii*. One Component of a Potential System for Reduction of Methemerythrin in Vivo

Sir:

Hemerythrin (Hr), the oxygen-carrying protein found in erythrocytes of sipunculan worms, is the counterpart to hemoglobin in mammalian erythrocytes. In contrast to hemoglobin, Hr contains a non-heme binuclear iron center as the oxygen-binding site.[1,2] This site can be stabilized in four distinct states: [Fe(II),Fe(II)](deoxy), [Fe(III),Fe(III)–O_2^{2-}](oxy), [Fe(II),Fe(III)](semi-met), and [Fe(III),Fe(III)](met). All four states exhibit antiferromagnetic coupling between iron atoms, which is mediated by an oxo or hydroxo bridge.[3-5] Up to now only the former two states have been established as physiologically relevant, since only these two have been implicated in reversible binding of O_2. Purified Hr from erythrocytes of the sipunculid *Phascolopsis gouldii* undergoes autooxidation according to the reaction

$$[Fe(III),Fe(III)–O_2^{2-}](oxy) + 2H^+ \rightarrow [Fe(III),Fe(III)](met) + H_2O_2$$

At 25 °C, pH 7.0, and 0.3 M Cl^-, $t_{1/2}$ for autooxidation is 18.5 h.[1] However, very little metHr is found in freshly isolated erythrocytes. Therefore, a system apparently exists within the erythrocyte that either prevents or reverses autooxidation.

Hemoglobin also undergoes autooxidation to a met form. In normal mammalian erythrocytes methemoglobin accounts for less than 1% of the total hemoglobin.[6,7] This low steady-state level is maintained by a reductase system in which electrons are transferred to methemoglobin in the sequence NADH → cytochrome b_5 reductase → cytochrome b_5 → methemoglobin.[8,9]

Despite the differences between mammalian and sipunculan erythrocytes, we have discovered what appears to be a similar system in *P. gouldii*. Herein we report preliminary characterization of a cytochrome b_5 (*P. gouldii* cyt b_5) isolated from the soluble fraction of *P. gouldii* erythrocytes and the possible role of *P. gouldii* cyt b_5 in reduction of metHr in vivo. Table I compares the properties of *P. gouldii* cyt b_5 with those of human erythrocyte cyt b_5.[10] As can be seen, these properties are quite similar. Figures 1 and 2 show the absorption and EPR spectra, respectively, of *P. gouldii* cyt b_5. The EPR parameters are typical of proteins having low-spin ferric heme with axial bis(histidine) ligation.[12] *P. gouldii* cyt b_5 in either the oxidized or reduced form

Table I. Comparison of Properties of Cytochromes b_5 from Human and *P. gouldii* Erythrocytes

	human[a]	*P. gouldii*[b]
mol wt	13 700	14 000[d]
pI	4.3	3.8
EPR *g* values (oxidized)	3.03, 2.21, 1.39[c]	3.07, 2.22, 1.4
Soret max (oxidized; reduced), nm	412; 423	412; 422
α-band max (reduced), nm	556	555
β-band max (reduced), nm	526	526

[a] Reference 9. [b] This work. [c] Reference 13. [d] Determined in 6 M guanidine hydrochloride by HPLC using an Altex Spherogel-TSK 300-PW column and commercial samples of *C. pasteurianum* ferredoxin (6000), horse heart cytochrome *c* (13 000), and sperm whale myoglobin (17 800) as molecular weight markers.

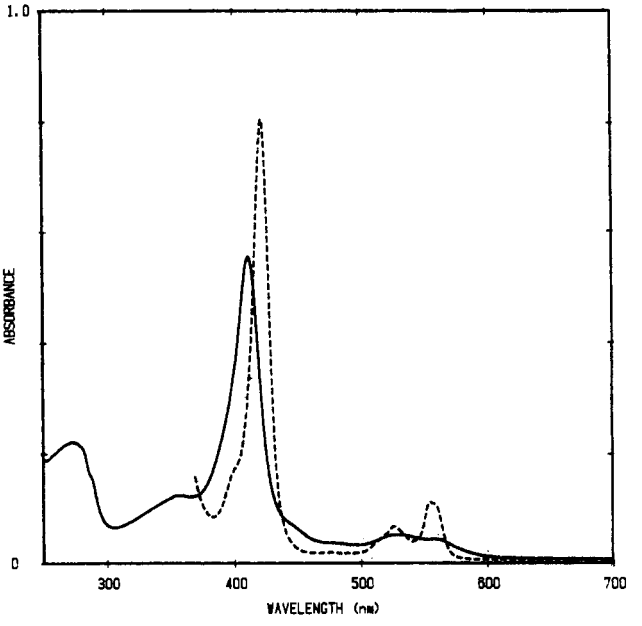

Figure 1. UV-visible spectra of oxidized (—) and reduced (- -) *P. gouldii* cyt b_5.

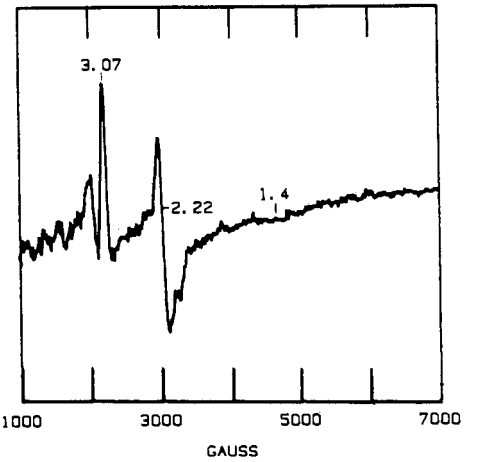

Figure 2. First-derivative EPR spectrum of *P. gouldii* cyt b_5. Spectral conditions: temperature, 4 K; frequency, 9.42 GHz; power, 20 mW; modulation, 16 G at 100 kHz; time constant, 0.15; gain, 3.2×10^4. Positions of the *g* values reported in Table I are indicated.

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