

oxidants, competing ligand oxidation reactions apparently take place, although no pure products could be isolated to confirm this.

One feature that stands out in this series of Fe(III) complexes is the effect of ring size and axial donor on the spin state of the Fe(III) ion. A vivid example of the effect of the axial donor is exhibited by the two 15-membered ring *p*-quinonate(2-)-bridged dimer derivatives. The Fe(III) centers in the benzoquinone derivative are in the $S = 5/2$ ground spin state, while the Fe(III) centers in the tetrachlorobenzoquinone derivative are in the $S = 3/2$ ground state. Interestingly, these *p*-quinonate(2-) derivatives may possibly serve as models for the cytochrome type dehydrogenases in which a coenzyme, a *p*-quinone derivative, is known to donate electrons to the iron in the heme group of the cytochrome.

In light of our results and those of other workers,⁶ it is likely that the $S = 3/2$ ground spin is common for Fe(III) bound to N_4X donor sets. Further, this $S = 3/2$ ground state may be relevant for intermediates in the biological reactions of heme iron derivatives, such as the cytochromes.^{9c}

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Registry No. **1a**, 62158-22-9; **1b**, 62158-23-0; **1c**, 62158-25-2; [Fe(Me₂[14]tetraenatoN₄)Cl], 91294-67-6; [Fe(Me₂[14]tetraenatoN₄)Br], 91294-68-7; [Fe(Me₂[14]tetraenatoN₄)I], 91294-69-8; [Fe(Me₂[14]tetraenatoN₄)(NO)], 91294-70-1; [Fe(Me₂[14]tetraenatoN₄)(NCS)], 91294-71-2; [[Fe(Me₂[14]tetraenatoN₄)₂Q], 91294-72-3; [[Fe(Me₂[14]tetraenatoN₄)₂QCl], 91294-73-4; [Fe(Me₂[15]tetraenatoN₄)Cl], 91294-74-5; [Fe(Me₂[15]tetraenatoN₄)Br], 91294-75-6; [Fe(Me₂[15]tetraenatoN₄)I], 91294-76-7; [Fe(Me₂[15]tetraenatoN₄)(NO)], 91294-77-8; [Fe(Me₂[15]tetraenatoN₄)(NCS)], 91294-78-9; [[Fe(Me₂[15]tetraenatoN₄)₂Q], 91294-79-0; [[Fe(Me₂[15]tetraenatoN₄)₂QCl], 91294-80-3; [Fe(Me₂[16]tetraenatoN₄)Cl], 91294-81-4; [Fe(Me₂[16]tetraenatoN₄)I], 91294-82-5; [[Fe(Me₂[16]tetraenatoN₄)₂Q], 91310-94-0; [[Fe(Me₂[16]tetraenatoN₄)₂QCl], 91310-95-1.

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Reactions of Metal Atoms with Alkynes. 2.¹ Cocondensation Reactions of Germanium and Tin Atoms with Acetylene and Formation of Integral Metal-Acetylene Polymers

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Germanium and tin vapors react with acetylene in a stationary metal atom reactor to form integral acetylene-metal copolymers of reproducible stoichiometry, i.e. (C₂H_{2.7}Ge_{0.72})_x and (C₂H_{2.6}Sn_{0.70})_x. The metal is incorporated as M(II) and M(IV) species, and the resultant materials are air-sensitive and possess moderate free-radical concentrations but are nonconducting under normal pressed-powder conditions.

Introduction

In 1978 we reported that germanium vapor, when cocondensed with either propyne or but-2-yne in a synthetic-scale metal atom reactor, yielded high polymers (containing *incorporated germanium*) that were unreactive toward concentrated hydrochloric acid and room-temperature aqua regia and were insoluble in common organic solvents.¹ Due to the difficulty in characterizing these polymeric substances, no further work has been performed on either the propyne or but-2-yne reaction products.

Recently, the ability of (suitably doped) polyacetylenes to conduct electric current² has rekindled our interest in the interaction of metal vapors with alkynes. Specifically, we wished to investigate the polymerization of acetylene by germanium and tin vapors to determine (a) whether polymerization would occur and (b) whether the metal atoms would simultaneously act as polymerization initiators and polymer dopants. Indeed, we have found that both germanium and tin atoms/vapors react with acetylene in a unique manner when

compared to other metal vapors, producing interesting new materials. Herein we report the synthesis and properties of these polymers.

Experimental Section

Metal Atom Reactor. The design of the simple metal atom reactor, which is the basis for the reactions herein described, has been detailed elsewhere.³ Due to the volatility of acetylene, however, the "shower head" ligand inlet was modified to permit more efficient metal-acetylene mixing during the cocondensation process. This modified system is fashioned with ~1-mm holes that extend about 20 mm up from the bottom of the shower head. This small area of holes (the normal area of holes extends about 90 mm up from the bottom of the shower head) was necessitated by the volatility of the gaseous acetylene being inlet to the reaction zone. With this design, condensation of the acetylene on the reactor walls is very efficient, ensuring that the low pressures necessary for a successful metal atom reaction are easily maintained and that the acetylene remains in the reactor and is not pumped away during the course of a reaction. A silicone oil bubbler fitted with a needle valve is used to control the acetylene inlet rate.

Acetylene Purification. *Caution!* Acetylene gas should always be handled in glass and/or aluminum, stainless-steel, or other nonreactive tubing. Prolonged contact with copper tubing is especially to be avoided. Handling of acetylene at greater than atmospheric pressure is also to be avoided, since even small pressures above atmospheric pressure (as little as 30 psia in a 1-in. tube, or smaller over-pressures in larger volumes) can cause spontaneous deflagration or detonation.⁴ Care must be taken to ensure that the final pressure of acetylene gas

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Table I. Elemental Analysis Results

sample	% C	% H	% M	total %	mol ratio ^a
Ge	29.14	3.70	63.56	96.40	2.00:3.02:0.72
Ge ^b	30.50	3.62	66.88	101.00	2.00:2.83:0.73
	30.57	3.60	66.15	100.32	2.00:2.81:0.72
Ge	30.29	3.44	67.31	101.04	2.00:2.71:0.74
calcd ^c	(30.38)	(3.51)	(66.11)	(100.00)	(2.00:2.75:0.72)
calcd ^c	(30.85)	(3.88)	(65.26)	(100.00)	(2.00:3.00:0.70)
Sn	14.93	1.67	73.01	89.61	2.00:2.67:0.99
Sn	18.24	2.03	73.88	94.15	2.00:2.65:0.82
Sn ^b	21.45	2.32	75.18	99.95	2.00:2.57:0.71
	21.75	2.39	75.46	100.60	2.00:2.62:0.70
calcd ^c	(21.89)	(2.39)	(75.72)	(100.00)	(2.00:2.60:0.70)
calcd ^c	(21.81)	(2.75)	(75.44)	(100.00)	(2.00:3.00:0.70)

^a Mole ratio C:H:M. ^b Duplicate analyses on the same sample.
^c Based upon the indicated mole ratio.

in the reactor upon warming is less than atmospheric pressure.

Commercial acetylene⁵ was purified by variations on published procedures.^{4,6} The acetylene, passed through a regulator (15 psig maximum output) from the cylinder, was entrained through (a) a silicone oil bubbler, (b) a tower of 8–14 mesh activated alumina, (c) a concentrated sulfuric acid bubbler, (d) a tower of 8–14 mesh soda lime, and (e) a trap at –78 °C. Empty flasks separated each purification step to act as ballast and to prevent back-flush and mixing of the purification train components. After passage through the purification train, the acetylene was freeze/thaw degassed and stored in a flask with a volume of approximately 3500 mL.

Solvent Purification. Reagent grade toluene and pentane used to slurry out the insoluble products of the metal atom reactions were freshly distilled under nitrogen from a sodium/benzophenone mixture (benzophenone ketyl).

Preparation of the Germanium–Acetylene Polymer. In a typical reaction, 0.642 g (8.85 mmol) of germanium metal vapor was cocondensed with 0.146 mol of acetylene gas over a period of approximately 2.5 h. At the end of this time, the reactor was isolated from dynamic vacuum, the Dewar of liquid nitrogen was removed, and the reactor was allowed to warm to room temperature under a static vacuum. Immediately upon removal of the Dewar, the matrix was pale yellow; as the matrix warmed, the color slowly darkened, changing from pale yellow to golden yellow to reddish-yellow to red to red-brown; the polymer is dark yellow- to red-brown at room temperature and spontaneously peeled off the reactor walls in thin, flexible films.

When the reactor had warmed to room temperature (approximately 30 min), the unreacted acetylene was recondensed back into the storage bulb and degassed, and the amount of acetylene in the bulb was measured (0.137 mol of acetylene unreacted after reaction; 8.80 mmol of acetylene consumed).

The reactor was filled with dry nitrogen, and under a flush of nitrogen, 150 mL of dry toluene was added via syringe. The insoluble polymeric product, as a slurry in toluene, was siphoned out of the reactor, under nitrogen, into a Schlenk tube, the tube was capped, and the toluene removed from the polymer in vacuo. The dry product is a yellow-brown powder, yield 0.646 g based on germanium vaporized and an approximate formula of (C₂H₃Ge_{0.7})_x (vide infra) (66%).

Preparation of the Tin–Acetylene Polymer. In a typical reaction, 0.438 g (3.69 mmol) of tin metal vapor was cocondensed with 0.137 mol of acetylene gas over a period of approximately 2 h. After this time, the reactor was isolated from dynamic vacuum, the Dewar of liquid nitrogen was removed, and the reactor was allowed to warm to room temperature under a static vacuum. Immediately upon removal of the Dewar, the matrix was red-gold and darkened upon warming, until at room temperature the color was dark brown.

Workup of the reaction was the same as for the germanium–acetylene polymer. The amount of acetylene consumed in this typical reaction was 0.55 mmol. After the product had been slurried out of the reactor with approximately 150 mL of dry toluene and dried in

Table II. Electron Spin Resonance Data

	g	area, ^a %		spin concn, spins/g
		ref ^b	sample	
Ge ^{c,d}	2.0035	5041.0 (±1.5)	6185.4 (±1.0) (0.0573 g)	6.49 × 10 ¹⁷
Ge ^{c,e}	2.0031	5174.9 (±2.1)	5835.7 (±1.0) (0.0483 g)	1.40 × 10 ¹⁷
Sn ^{d,f}	2.0012	5022.6 (±1.4)	607.5 (±3.2) (0.0617 g)	2.97 × 10 ¹⁵
Sn ^{e,f}	2.0012	6319.2 (±1.6)	1039.9 (±3.3) (0.0681 g)	1.14 × 10 ¹⁴

^a Arbitrary units. Percent error is for the standard deviation of five determinations. ^b At a concentration of 3.03 × 10¹⁶ spins. ^c Germanium–acetylene polymer. ^d Handled under nitrogen. ^e Exposed to air for 8 h. ^f Tin–acetylene polymer.

vacuo, it was a dark brown powder, yield 0.170 g based on tin vaporized and an approximate formula of (C₂H₃Sn_{0.7})_x (vide infra) (29%).

Elemental Analyses. Analyses were performed by (a) Galbraith Laboratories, Inc., Knoxville, TN, (b) Dornis and Kolbe Mikroanalytisches Laboratorium, 4330 Mülheim a. d. Ruhr 1, West Germany, and (c) Schwarzkopf Microanalytical Laboratory, Woodside, NY. The results are listed in Table I.

Infrared Spectra. All infrared spectra were recorded on a Beckman IR-12 infrared spectrophotometer, as KBr pellets, from 300 to 4000 cm⁻¹.

Visible/Ultraviolet Spectra. All UV/vis spectra were recorded on a Cary 14 recording spectrophotometer in the visible region from 8000 to 3500 nm and in the near-ultraviolet region from 3500 to 2000 nm. Because of the insolubility and/or air sensitivity of these polymers, the spectra were obtained as mineral oil mulls. The polymer samples were ground in mineral oil (previously dried over sodium metal and degassed) in much the same manner as that employed for the preparation of samples for infrared spectroscopy.⁷ The mull samples were then coated on (previously dried) filter paper, cut to fit into a quartz cuvette. The coated filter paper was placed in a quartz cuvette and pressed against one of the inner clear walls, where it was held in place by the adhesion of the mineral oil surface tension. Spectra of the polymers were recorded in double-beam mode vs. a mineral oil/filter paper/cuvette blank.

In all cases, the germanium–acetylene and tin–acetylene polymers (whether handled under nitrogen or exposed to air) exhibited only an extremely broad, featureless absorption, extending from the near-infrared (8000 nm) to beyond the near-ultraviolet (2000 nm) regions. No attempt was made to quantitate this absorption, due to difficulties in determining the concentration of the solid in oil suspensions.

Electron Spin Resonance Spectra. A preliminary investigation of the ESR properties of the germanium– and tin–acetylene polymers was performed on a Varian Model V4500 EPR spectrometer. This spectrometer operates in the X-band, ~9.5 GHz. The results of the investigation indicated that both polymers contained unpaired electrons; a strong, broad absorption was recorded for the germanium–acetylene polymer, and a weaker, somewhat asymmetric absorption, for the tin–acetylene polymer. Exposure to air for 24 h caused all ESR absorptions to disappear.

A much more detailed investigation of the ESR properties of these polymers was performed on a Bruker ER-420 electron resonance spectrometer, also operating in the X-band (9.68 GHz). The weighed polymer samples, handled under dry nitrogen, were sealed under vacuum in quartz ESR tubes; their spectra were recorded in the double-cavity operation mode vs. a known quantity (3.03 × 10¹⁶ spins) of diphenylpicrylhydrazine (dpph).

In order to determine the *g* values of the polymer radicals, the *g* value of dpph,⁸ 2.0037 ± 0.0002, was used as the reference to calibrate the spectrum. The calculation of the spins per gram of polymer sample required the determination of the area of the first-derivative curves above and below the origin line. These calculations were performed

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Table III. Tin-119m Mössbauer Data

sample no.	isomer shift, mm/s	quad split, mm/s	line width, mm/s
1 ^a	1.03 ± 0.02	1.99 ± 0.04	1.04 ± 0.04
	2.60 ± 0.02	2.58 ± 0.04	1.21 ± 0.04
2 ^a	0.98 ± 0.02	1.96 ± 0.04	1.36 ± 0.04
	2.71 ± 0.02	2.56 ± 0.04	1.54 ± 0.04
3 ^b	-0.09 ± 0.03		1.55 ± 0.03
	2.96 ± 0.03	2.34 ± 0.05	1.74 ± 0.03

^a Handled under nitrogen. ^b Exposed to air to oxidize sample.

Table IV. Conductivity Data for Polymers

	Ge-HC≡CH	Sn-HC≡CH
pellet size, cm	0.16	0.16
	0.0015	0.0021
probe size, cm	1.0	1.0
R_{av} , ^a Ω	>10 ⁹	>10 ⁹
σ , ^b Ω ⁻¹ cm ⁻¹	<4 × 10 ⁻⁶	<3 × 10 ⁻⁶
oxidn		
20 min	no change ^c	no change ^c
24 h	no change	no change
7 days	no change	no change

^a Average resistance at different applied currents; instrument limit 10⁹ Ω. ^b Conductivity. ^c In conductivity, from that of nonoxidized sample.

on an Apple II computer equipped with a Graphics Tablet according to the procedures described in the operations manual and instructions for the computer and tablet. Each area was measured five times. All the pertinent ESR results have been listed in Table II.

Mössbauer Spectra. Tin-119m Mössbauer spectra were recorded, as described elsewhere,⁹ at 77 K on a Ranger Engineering constant-acceleration spectrometer equipped with a proportional counter, using Ca¹¹⁹SnO₃ as the γ -ray source and Ca¹¹⁹SnO₃ as the zero isomer shift reference. Table III lists the data.

The spectra for the tin-acetylene polymer handled under nitrogen are best fit as two doublets with an overlapping line and, within experimental error, are identical, even though they are from two different metal vapor reactions.

Conductivity Measurements. Measurements of the pressed-powder conductivities of the germanium- and tin-acetylene polymers, except oxidations, were performed in an argon atmosphere drybox.

A dry, powdered sample of polymer was compressed into a pellet under approximately 10 000 lb/ft² pressure and then cut into a rectangular shape. Platinum wires were attached to the sample, by using either a pressure contact or Electrodag adhesive. A four-probe configuration¹⁰ was used in order to minimize or eliminate errors due to contact resistances between the platinum wires and the sample. The actual measurement of potential (in volts) was performed at direct currents of between 0.05 and 0.10 mA, either positive or negative. Within experimental error, measurements at different applied currents were the same. Conductivity, σ , is equal to c/abR , with values as listed in Table IV.

Thermal Decomposition Studies. Neither the germanium-acetylene polymer nor the tin-acetylene polymer nor the air-exposed analogues of either polymer exhibited any signs of melting up to 300 °C. However, some darkening of the powdered samples did begin at approximately 75 °C.

In order to investigate the characteristics of the polymers when heated in a static vacuum, thermal decomposition studies were carried out. The pyrolysis cell used for these studies was made of borosilicate glass with a volume of approximately 15 mL and was equipped with a high-vacuum stopcock and an outlet tube of the proper diameter to mate with the mass spectral inlet port.

Weighed samples of the polymers were loaded into the pyrolysis cell in a dry-nitrogen glovebox. Outside of the glovebox, the samples were evacuated and placed in a mineral oil bath preheated to 50 °C, where they remained for 30 min. At the end of this time, the samples were removed from the mineral oil bath and cooled. The gases released

by heating were analyzed in a Finnegan mass spectrometer using electron ionization at an electron energy of 20 eV, with an electron current of 0.1 A. After the mass spectra of the samples had been recorded, the cells were again evacuated and heated in the (preheated to the next higher temperature) mineral oil bath for 30 min. Each sample was heated to 50, 100, 150, 200, and 250 °C, and the gases evolved after each heating were analyzed by mass spectrometry.

Decomposition of the Germanium-Acetylene Polymer with Chlorine Gas. In an attempt to chemically decompose a sample of the germanium-acetylene polymer, a decomposition study with chlorine gas was attempted. The total product of a metal atom cocondensation reaction of germanium and acetylene was slurried in pentane, a magnetic stir bar was added under a nitrogen purge, and the flask was attached to a vacuum line. The slurry was degassed and cooled with a rock salt/ice/water bath to -2 °C. Over a period of 9.5 h, approximately 0.1 mol of chlorine gas was added to the slurried polymer. Initially, the polymer was red- to yellow-brown, but the color slowly lightened, finally becoming a snowy white. After the addition of the chlorine gas, the stirred slurry was allowed to slowly warm to room temperature and was then stirred overnight at room temperature. After this time period, the volatile products were removed in vacuo from the remaining white, insoluble, flocculent solid and analyzed by gas chromatography and gas chromatography/mass spectrometry.¹¹

GC/MS and gas chromatography (10-ft SE-30 column, 95 °C, 60 mL/min He flow rate, thermal conductivity detection) of the chlorine decomposition reaction products yielded evidence for 10 products, two major ones being trichloroethylene and pentachloroethane. Known compounds that did *not* match any of the unknown peaks included *cis*- and *trans*-1,2-dichloroethylene and 1,1,2,2-tetrachloroethane, 1,2-dichloroethane, and dichloro- and trichloromethane.

Results

Reaction Conditions and Elemental Analyses. The design of the experiments in which either germanium or tin atoms were cocondensed with acetylene gas allowed an acetylene to metal mole ratio of approximately 15:1 to 40:1 during the codeposition experiments. Under conditions such as these, in which the substrate was in excess, the probability that every metal atom reaching the reaction zone contacts at least one substrate molecule immediately is very high.

The first indications of the type of reaction taking place when either germanium or tin atoms are cocondensed with acetylene can be ascertained by plotting the amount of metal vaporized vs. the amount of acetylene consumed for the germanium-acetylene (Figure 1) and tin-acetylene (Figure 2) reactions. Although the plots contain some scatter (the equations for the lines calculated through linear-regression least-squares analysis have a coefficient of determination, r^2 , of approximately 0.8), they indicate a definite linear relationship between the amount of metal vaporized and the amount of acetylene consumed. This linear relationship eliminates the possibility of catalytic polymerization of acetylene by either germanium or tin atoms.

If the approximation is made that 75% of the metal vaporized actually reached the reaction zone and became incorporated into the metal-acetylene polymer, the dashed lines result. The slopes of these lines, 1.303 and 0.781 for the germanium- and tin-acetylene plots, respectively, indicate that within experimental error every metal atom reacts with about one acetylene molecule upon cocondensation.

The data received from the elemental analyses detailed in Table I further indicate that under the experimental conditions wherein a large excess of acetylene is cocondensed with either germanium or tin atoms, a product is formed with an elemental analysis, which, although nonstoichiometric, is very nearly invariant, even for samples from different reactions. For the germanium-acetylene polymer, the analyses indicate

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(11) GC/MS analyses performed by Dr. G. Groenewold, Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, NB.

a formula of $(C_2H_{2.7}Ge_{0.72})_x$, and for the tin-acetylene polymer, the analyses indicate a formula of $(C_2H_{2.6}Sn_{0.70})_x$.

Elemental analyses for doped polyacetylenes^{2a-c} are commonly expressed in units of $(CH)_x$, e.g. $[CH(AsF_5)_{0.10}]_x$. If the analyses for the germanium- and tin-acetylene polymers are also expressed in this manner, the results become $[CH(GeH)_{0.36}]_x$ and $[CH(SnH)_{0.35}]_x$, approximately. Dopant amounts of 0.36 and 0.35 are very similar to values found for polyacetylenes doped with lithium (0.30) and sodium (0.21–0.28).^{2c} However, it must be emphasized that these analytical formulas *do not* indicate anything about the *structure* of the polymer.

Infrared Spectral Data. (a) General Procedures. The infrared spectra of the polymers can give some information concerning the structure of the polymers, both for the samples handled under nitrogen and for those exposed to air. Recall, however, that assignments of the infrared absorption bands of polymers are at times difficult to make^{12a} and many still are the topics of debate,^{12b} especially for polymers containing organometallic groups.¹³ Except where specifically noted, the assignments made and discussed below are with reference to Maslowsky,¹⁴ Glockling,¹⁵ Carraher, Sheats, and Pittman,¹³ Nakamoto,¹⁶ and Nakanishi and Solomon.¹⁷

(b) Samples Handled under Nitrogen. The infrared spectrum of the germanium-acetylene polymer handled under nitrogen exhibits a very strong absorption at 639 cm^{-1} that is readily assignable¹⁴ as a $\nu(\text{Ge}-\text{C})$ stretching mode and fits well with data for germanium-vinyl stretches. The corresponding absorption of the tin-acetylene polymer occurs at 439 cm^{-1} and is very broad. Although approximately 50 cm^{-1} lower than reported¹⁴ ranges for $\nu(\text{Sn}-\text{C})$ stretching modes in tin-vinyl compounds, this strong, broad absorption is very probably due to $\nu(\text{Sn}-\text{C})$. Since the elemental analyses indicate that the polymers contain no oxygen, these absorptions are *not* due to $\nu(\text{Sn}-\text{O})$.

The germanium- and tin-acetylene polymers exhibit absorptions at, respectively, 2946 and 2941 cm^{-1} , which can be attributed to $\nu(\text{C}-\text{H})$. Both polymers exhibit absorptions in the range 1500 to 1350 cm^{-1} , which is the range where C-H in-plane bends of olefins and the C-H rocking modes of *cis* disubstituted olefins occur.^{17,18}

In the infrared spectrum of the germanium-acetylene polymer, additional absorptions occur that are not observed in the tin-acetylene polymer. At 998 and 732 cm^{-1} , absorptions appear that can be assigned^{17,18} to the C-H out-of-plane bending modes of, respectively, *trans* and *cis* disubstituted olefins. In addition, the absorptions at 2033 and 3285 cm^{-1} may be due to respectively $\nu(\text{C}=\text{C})$ and $\nu(\equiv\text{C}-\text{H})$, as has been found for molecular alkynyl-germanium compounds.¹⁹ Finally, the broad absorption at 1595 cm^{-1} is similar to that found in linear, conjugated polyolefins.¹⁷

(c) Samples Exposed to Air. The $\nu(\text{Ge}-\text{O})$ and $\nu(\text{Sn}-\text{O})$ absorptions in these polymers are, at first glance, straight-

forward in assignment. The germanium-acetylene polymer exposed to air exhibits a strong absorption at 659 cm^{-1} , and the spectrum of the corresponding tin-acetylene polymer has a distinctive, broad absorption at 549 cm^{-1} . However, the $\nu(\text{M}-\text{O})$ mode ranges overlap with the $\nu(\text{M}-\text{C})$ mode ranges.²⁰ Therefore, although it is tempting to simply assign these absorptions as the $\nu(\text{M}-\text{O})$ modes, the possibility exists, especially with the very broad absorption in the tin-acetylene polymer, that both $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{C})$ modes contribute to the absorptions.

Both spectra exhibit quite normal-appearing absorptions that can be assigned to $\nu(\text{C}-\text{H})$ in the region 3000 – 2850 cm^{-1} and to $\nu(\text{C}=\text{O})$ in the region 1700 – 1600 cm^{-1} . (The $\nu(\text{C}=\text{O})$ absorption in the tin-acetylene polymer is quite weak, however.) There are also indications of $\nu(\text{C}-\text{O})$ at 1265 cm^{-1} , and both spectra exhibit strong, broad $\nu(\text{O}-\text{H})$ absorptions (not due *solely* to adsorbed water on KBr) at 3400 cm^{-1} .

UV/Vis Spectral Data. The polymers, whether the germanium- or the tin-acetylene product, handled under nitrogen or air exposed, exhibit only an extremely broad, featureless absorption extending from the near-infrared to beyond the near-ultraviolet (8000 – 2000 nm) regions. Results similar to these were found by Evans and co-workers²¹ for the products of lanthanide metal atom/alkyne cocondensation reactions. The products of the lanthanide metal atom cocondensation reactions, however, were soluble, oligomeric organometallic complexes.

Electron Spin Resonance Spectral Data. The electron spin resonance spectra of undoped and AsF_5 -doped polyacetylene have been measured.²² For the undoped polymer, the g value was measured as 2.0026 with 1.44×10^{19} spins/g, or approximately one unpaired electron for every 3000 carbon atoms. When the undoped polymer was exposed to air or was doped, the number of unpaired electrons *increased* and the line width *decreased*. Short-term exposures to oxygen were reversible; oxygen adsorption became irreversible at longer exposure times.

For the germanium-acetylene polymer handled under nitrogen, the g value was measured as 2.0035 , with 6.49×10^{17} spins/g. This spin concentration translates to about one unpaired electron for every 20 000 carbon atoms. In the case of the tin-acetylene polymer handled under nitrogen, the g value was measured as 2.0012 , with 2.97×10^{15} spins/g, or about one unpaired electron for every 3 500 000 carbon atoms. Both germanium- and tin-acetylene polymers lose all ESR signal after long exposures to oxygen; short exposures caused a *decrease* in the number of unpaired electrons, and the line width *decreased*. In addition, oxygen exposure caused an irreversible change, independent of exposure time.

Mössbauer Spectral Data. The data from the tin-119 m Mössbauer spectra indicate that the tin in the acetylene polymer is in two different formal oxidation states. In the spectra of the polymer handled under nitrogen (which are identical, even though arising from two different metal atom reactions), the doublet centered at 1.01 mm/s (average) is due to the presence of tin(IV) while the doublet centered at 2.66 mm/s (average) is due to tin(II) species. These assignments are based upon the value of 2.65 mm/s as the formal division between tin(II) and tin(IV).²³ All compounds formally

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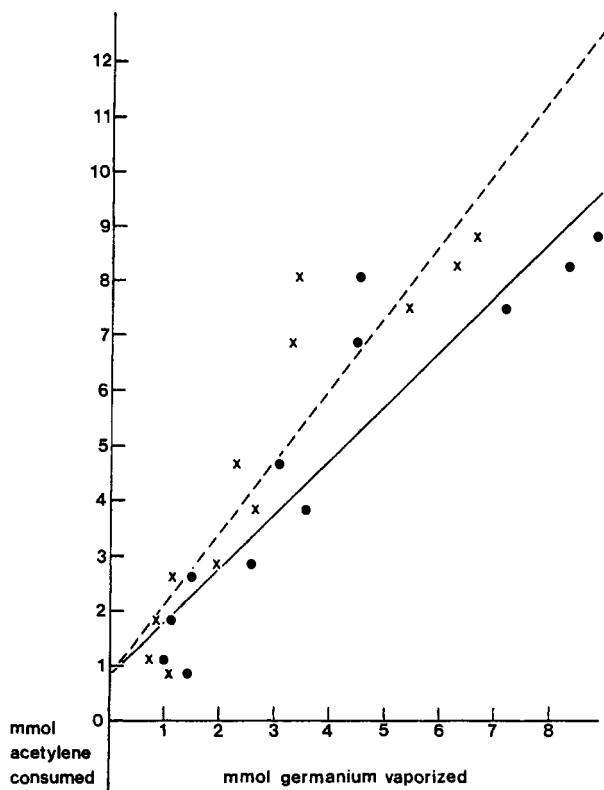


Figure 1. Plot of the mmol of germanium vaporized vs. the mmol of acetylene consumed in the reactions of metal vapors with acetylene. Solid symbols represent points plotted by using the actual mass of metal vaporized; X symbols are plotted by using 75% of the actual mass of metal vaporized. The equations were calculated through linear-regression least-squares analyses; the solid line refers to the solid symbols, and the dashed line refers to the X symbols. Equations: solid line, $y = 0.978x + 0.904$, $r^2 = 0.838$; dashed line, $y = 1.303x + 0.904$, $r^2 = 0.838$.

recognized as tin(IV) fall below 2.65 mm/s, and those assigned as tin(II) appear at or above that value.

The absence of a strong Mössbauer spectrum at ambient temperatures in the samples handled under nitrogen eliminates the possibility that α -tin, β -tin, or tin(IV) oxide is present in the polymer before exposure to air. These three materials exhibit strong absorptions at ambient temperatures.²³ Exposure of the polymer to air converted both the tin(II) and tin(IV) materials to SnO_2 ; conversion of the tin(II) material first to tin(IV) material and then conversion to SnO_2 was ruled out as a possibility through observation of the Mössbauer absorptions during oxidation.

Conductivity Data. Under the pressed-powder methods used in the determination of the conductivity of the germanium- and tin-acetylene polymers, the polymers exhibit only *insulating* behavior. This result is not necessarily surprising, however, considering the low unpaired electron (spin) concentration results found in the electron spin resonance experiments. Air exposure had no effect within the instrumental limits.

Decomposition Studies. The initial attempt to determine the structure of the germanium- and tin-acetylene polymers by chlorinative degradation was based on the reports that unsaturated organic groups attached to germanium could be cleaved under extremely mild conditions by halogens.¹⁵ Our data indicate that this is true, to a degree, for the germanium-acetylene polymer. The fact that no isotopic patterns assignable to germanium-containing compounds were found in the mass spectra of the chlorinated product mixture, however, indicates that only germanium-carbon bonds near the surface of the polymer were cleaved. Under our conditions,

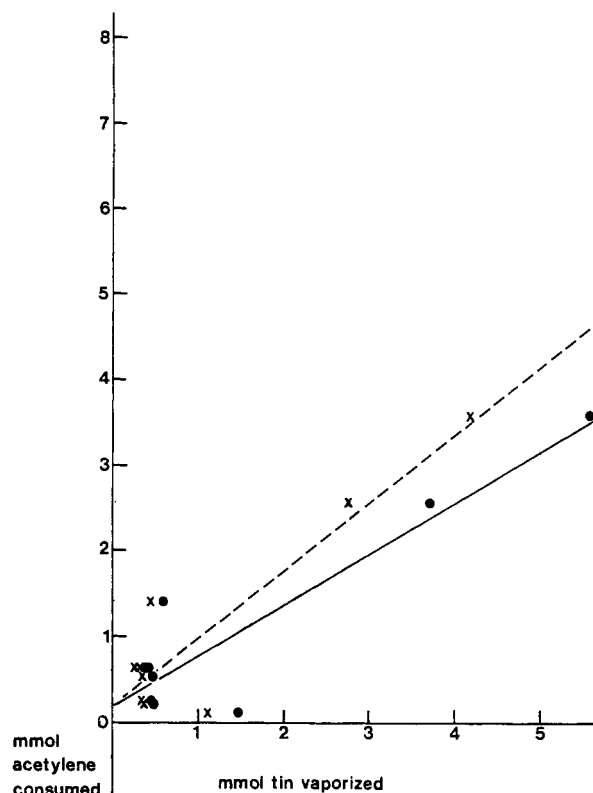
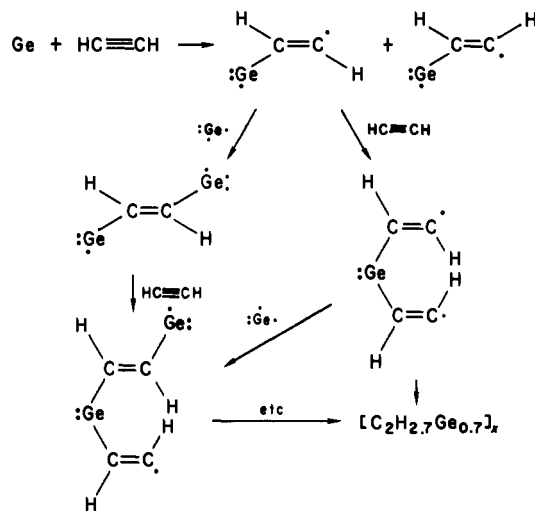


Figure 2. Plot of the mmol of tin vaporized vs. the mmol of acetylene consumed in the reactions of tin vapor with acetylene. For explanation of symbols, see Figure 1. Equations: solid line, $y = 0.586x + 0.225$, $r^2 = 0.831$; dashed line, $y = 0.781x + 0.225$, $r^2 = 0.831$.

Scheme I



the major reaction may be chlorine addition to the polymer without a large degree of bond cleavage. The two chlorinated products definitely identified, trichloroethylene and pentachloroethane, support a surface-only type of reaction, since these two products could arise from the germanium-carbon bond cleavage of a surface species such as [(bulk polymer)- $\equiv\text{Ge}-\text{C}\equiv\text{C}-\text{H}$], followed by addition of Cl_2 .

The major peaks in the mass spectra of the pyrolyses of the polymers correspond to H_2O (m/e 18), C_2H_2 (m/e 26), C_2H_4 (m/e 28), CO_2 (m/e 44), butadiene, C_4H_6 (m/e 56), benzene (m/e 78), and residual toluene (m/e 92). In general, the mass spectra of the air-exposed germanium- and tin-acetylene polymers are similar, but the tin-acetylene polymer releases a specific product (such as H_2O or CO_2) in larger amounts at a lower temperature than does the germanium-analogue. In the same way, the tin-acetylene polymer releases large

quantities of acetylene, while the germanium analogue does not. These results point out the enhanced reactivity and diminished stability of the tin polymer over the germanium analogue.

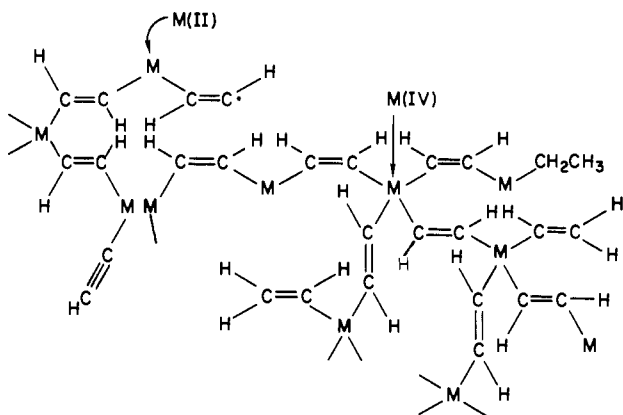
Discussion

It is clear that the cocondensations of germanium or tin atoms with acetylene produce air-sensitive, polymeric products of reproducible stoichiometry, i.e., $(C_2H_{2.7}Ge_{0.72})_x$ and $(C_2H_{2.6}Sn_{0.70})_x$. The compounds are weakly paramagnetic, with about one unpaired electron for every 20 000 and 3 500 000 carbon atoms, respectively. They react with oxygen irreversibly, and the oxidized polymers no longer exhibit an ESR spectrum. Mössbauer spectra indicate that the tin-acetylene polymer contains both tin(II) and tin(IV) species but that no α -tin, β -tin, or SnO_2 is present before exposure to air.

The pressed-powder conductivities of the polymers are very low, indicating that although germanium and tin atoms do react with acetylene to form a polymer, doping to the semi-conducting or metallic state does not occur.

Thermal decomposition studies indicate that the tin-acetylene polymer is less thermally stable than the germanium analogue. This parallels the air sensitivity of the two polymers. Peaks in the mass spectra corresponding to acetylene, ethylene, butadiene, butenes, benzene, and residual toluene solvent have been identified.

Taking these data together, the best average structure for these polymers may be



high polymer, cross-linked, with occasional defects, resulting in trapped radicals; note C_2H , C_2H_3 , and C_2H_5 units

With regard to the unique nature of Ge and Sn atoms for these copolymerization reactions, we have investigated many other metals such as V, Cr, Mn, Fe, Co, Ni, Pb, and others. Only Ge and Sn yielded these polymeric materials. The electronic configurations of the ground-state atoms as 3P di-radical species may account for this uniqueness.²⁴ A possible reaction mode is shown in Scheme I. We carried out a Ge vapor/ $HC\equiv CH$ deposition at 10 K under matrix-isolation conditions²⁵ and observed no changes using infrared as a probe.²⁶ We hope to extend these studies to ESR soon.

Acknowledgment. We thank J. J. Zuckerman and T. S. Dory for Mössbauer studies, A. G. MacDiarmid and S. Porter for conductivity studies, M. B. Jones for ESR assistance, A. S. Eriksson for technical assistance, and the Phillips Petroleum Co. Foundation for a fellowship for R.W.Z. The support of the National Science Foundation is acknowledged with gratitude.

Registry No. Germanium, 7440-56-4; tin, 7440-31-5; acetylene, 74-86-2.

Supplementary Material Available: Listings giving germanium vaporized vs. acetylene consumed (Table V), tin vaporized vs. acetylene consumed (Table VI), and infrared absorptions for the metal-acetylene polymers (Table VII), ESR spectrum of the Ge-acetylene polymer (Figure 3), and Mössbauer spectra of Sn-acetylene polymers (Figures 4-6) (7 pages). Ordering information is given on any current masthead page.

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Notes

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Synthesis and Characterization Studies on New Ethylenediamine-*N,N'*-diacetate Complexes of Cobalt(III)¹

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Numerous complexes² of the sort $[Co(EDDA)(L)]^{\pm}$ (EDDA = ethylenediamine-*N,N'*-diacetate ion (symmetrical

EDDA)), where L = CO_3^{2-} , ox, mal, and en, and $[Co(EDDA)(X)_2]^{\pm}$, where X = Cl^- , NO_2^- , and H_2O , have been thoroughly studied by Legg et al.³ and Garnett and Watts.⁴ Both *s-cis* and *uns-cis* isomers were obtained and characterized by using ion-exchange, NMR, and UV-vis techniques; *s-cis* (symmetrical *cis*) and *uns-cis* (unsymmetrical *cis*) describe geometrical configurations for EDDA. In each case the two coordination positions not occupied by EDDA are *cis* to one other. In the *s-cis* configuration the two EDDA acetate arms are *trans*, while in *uns-cis* the acetate arms are *cis*.⁵ By

(1) Reported at the 185th National Meeting of the American Chemical Society, Seattle, WA, March 20-25, 1983. Taken in part from: Sigel, G. A. M.S. Thesis, Western Washington University, 1982.

(2) Abbreviations: U-EDDA = ethylenediamine-*N,N'*-diacetate, EDDA = ethylenediamine-*N,N'*-diacetate, ox = oxalate, mal = malonate, en = ethylenediamine, tn = 1,3-propanediamine (trimethylenediamine).
 (3) Coleman, P. F.; Legg, J. I.; Steele, J. *Inorg. Chem.* **1970**, *9*, 937.
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