an aqueous solution of $[Co(pyaneN_5)Cl]^{2+}$ followed by addition of a concentrated $NaClO_4$ solution produced orange-gold crystals which were recrystallized from hot water.

$[Fe(pyaneN_5)(Cl)_2]PF_6$. To 0.74 g (3.8 mmol) of anhydrous iron(II) chloride dissolved in ethanol under an inert atmosphere was added 1.1 g (3.8 mmol) of free ligand in ethanol. The reaction mixture was heated for 15 min at 60° and then exposed to air. The solution changed in color from yellow to yellow-green within minutes. One equivalent (0.62 g) of NH_4PF_6 was added and the solution was filtered to remove any iron oxides. The volume of the filtrate was reduced until the yellow product began to form. The crystals were washed with ethanol and dried *in vacuo* at 60°.

$[Fe(pyaneN_5)(Br)_2]PF_6$. The same procedure as given above for the dichloro derivative was followed, except that anhydrous iron(II) bromide was used.

$[Fe(pyaneN_5)(NCS)_2]PF_6$ and $[Fe(pyaneN_5)(N_3)_2]PF_6$. Two equivalents of LiNCS or LiN_3 dissolved in ethanol was added to a slurry of $[Fe(pyaneN_5)(Cl)_2]PF_6$ in ethanol. As the solution was heated, all of the solid dissolved to form a deep red solution. Upon reduction of volume and cooling, red crystals of $[Fe(pyaneN_5)(NCS)_2]PF_6$ or orange crystals of $[Fe(pyaneN_5)(N_3)_2]PF_6$ formed. The products were dried *in vacuo* at 60°.

$[Fe(pyaneN_5)(NO_3)_2]PF_6$. Two equivalents of $AgNO_3$ was added to an acetonitrile solution of $[Fe(pyaneN_5)(Cl)_2]PF_6$. The precipitate AgCl was filtered and the filtrate was reduced in volume until yellow crystals of $[Fe(pyaneN_5)(NO_3)_2]PF_6$ formed.

$[Fe(pyaneN_5)C_2O_4]PF_6$. One equivalent of $Li_2C_2O_4$ dissolved in water was added to an acetonitrile solution of $[Fe(pyaneN_5)Cl_2]PF_6$. Reduction of the solution volume induced precipitation of $[Fe(pyaneN_5)C_2O_4]PF_6 \cdot nH_2O$ which was dried *in vacuo* to give $[Fe(pyaneN_5)C_2O_4]PF_6 \cdot H_2O$.

$[Cu(pyaneN_5)](PF_6)_2$. Addition of 0.76 g (3.8 mmol) of $Cu(OAc)_2 \cdot H_2O$ to 2.0 g (3.8 mmol) of $pyaneN_5 \cdot 4HNO$, in water resulted in a deep blue solution. Addition of 1.24 g (7.6 mmol) of NH_4PF_6 induced crystallization of the deep blue product which was washed with ethanol and dried *in vacuo*.

Registry No. $[Ni(pyaneN_5)H_2O](PF_6)_2$, 54325-58-5; $[Ni(pyaneN_5)CH_3CN](PF_6)_2$, 54325-60-9; $[Ni(pyaneN_5)NCS](NCS)$, 54325-62-1; $[Ni(pyaneN_5)NH_3](PF_6)_2$, 54325-64-3; $[Ni(pyaneN_5)Cl]Cl$, 54325-65-4; $[Ni(pyaneN_5)Br]Br$, 54325-66-5; $[Ni(pyaneN_5)I]I$, 54325-67-6; $[Co(pyaneN_5)Cl](ClO_4)_2$, 54325-69-8; $[Co(pyaneN_5)Br](ClO_4)_2$, 54325-71-2; $[Co(pyaneN_5)I](I)_2$, 54325-72-3; $[Co(pyaneN_5)NCS](ClO_4)_2$, 54325-40-5; $[Co(pyaneN_5)N_3](ClO_4)_2$, 54325-42-7; $[Co(pyaneN_5)NO_2](ClO_4)_2$, 54325-44-9; $[Fe(pyaneN_5)Cl_2](PF_6)$, 54325-46-1; $[Fe(pyaneN_5)Br_2]PF_6$, 54340-23-7; $[Fe(pyaneN_5)(NO_3)_2]PF_6$, 54325-48-3; $[Fe(pyaneN_5)(NCS)_2]PF_6$, 54325-50-7; $[Fe(pyaneN_5)(N_3)_2]PF_6$, 54325-52-9; $[Fe(pyaneN_5)C_2O_4]PF_6$, 54325-54-1; $[Cu(pyaneN_5)](PF_6)_2$, 54325-56-3; $pyaneN_5 \cdot 4HNO_3$, 54293-31-1; $Mn(pydieneN_5)Cl_2$, 27577-84-0; $[Ni(pyaneN_5)H_2O]^{+3}$, 54325-32-5.

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Synthesis and Electrical Properties of Transition Metal Mercaptides of 1,4-Dimercaptobenzene[1]

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The synthesis of a number of new transition metal mercaptides of the ligand 1,4-dimercaptobenzene is reported. Several of these mercaptides, which are regarded as S-bridged polymers, behave like semiconductors within the temperature range investigated. An interesting result of the study is the relatively low electrical resistivity (ρ = 40 ohm cm at 25°) of the Cu(I) complex of composition $[CuSC_6H_4SCu]_n$. Copper thiophenolate, $[C_6H_5SCu]_n$, is also found to behave like a semiconductor, with an electrical resistivity of 5.1×10^4 ohm cm at 25°. The reaction of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) with Cu(I) complexes cleaves the Cu–S bonds and leads to the formation of the Cu(I) salt of the TCNQ radical anion, $Cu^+TCNQ\cdot^-$.

Introduction

Extensive studies of the coordination chemistry of unsaturated or aromatic 1,2-dithiol ligands have been reported,[2–5] and semiconductor behavior has been noted for transition metal complexes of α-dithiodiketones, dithiooxamide (rubeanic acid), and N-substituted dithiocarbamates.[6–8] However, no information is available concerning 1,4-dimercaptobenzene and other aromatic polythiols as potential ligands. We became interested in these ligands and their coordination polymers with the object of finding new thermally stable materials having semiconducting properties. The ligands chosen meet the requirements to form complexes with these properties. First, they are thermally stable and possess donor atoms separated by an aromatic ring. Second, each ligand can bind two metal atoms, and substantial back-coordination of the metal d electrons to the ligand-based antibonding orbitals as well as the formation of sulfur-bridged metal chains could facilitate electron transport. In this paper, we report the synthesis and the chemical and electrical properties of a number of new polymeric mercaptides of 1,4-dimercaptobenzene having the

Table I. Elemental Analyses and Physical Properties of the Transition Metal Mercaptides

				Analyses, %								
				C		H		S		Metal		
Entry	Complex	Solvent	Color	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Dec temp, °C
1	$[CuSC_6H_4S-]_n$	H_2O	Yellow-brown	35.39	35.42	1.96	2.06	31.46	31.56	31.18	31.01	>250
2	$Cu[SC_6H_4SCu]_3$[a]	$H_2O-NaOH-Na_2S_2O_4$	Yellow	32.04	32.21	1.78	1.88	28.51	28.78	37.67	37.70	>270
3	$[CuSC_6H_4SCu]_n$	2,4-Lutidine	Yellow	26.96	27.23	1.50	1.52	23.99	23.93	47.55	47.74	>330
4	$[CuSC_6H_4SCu]_n$	Solid state	Yellow	26.96	27.99	1.50	1.58	23.99	26.06	47.55	46.04	>330
5	$[AgSC_6H_4SAg]_n$	2,4-Lutidine	Yellow	20.25	20.45	1.12	1.01	18.02	17.85	60.61	60.51	N[b]
6	$[HgSC_6H_4S-]_n$	2,4-Lutidine	Yellow	21.15	21.30	1.17	1.19	18.82	18.72	58.86	58.84	285–290[c]
7	$[Pb-S-C_6H_4S-]_n$	H_2O-CH_3OH	Brown	20.74	21.01	1.15	0.79	18.45	18.45	59.65	59.58	>320
8	$[C_6H_5SCu]_n$	C_2H_5OH	Pale yellow	41.73	41.62	2.89	2.92	18.56	18.85	36.80	36.88	>280
9	$[NiSC_6H_4S-]_n$	THF	Black	36.23	36.60	2.01	2.24	32.24	32.56	29.52	28.49	>310

[a] Complex in entry 2 appears to be a 1:2 mixture of $[CuSC_6H_4SCu]_n$ (shown by the X-ray powder diffraction) and $[CuSC_6H_4S-]_n$, respectively. [b] No decomposition up to 350°. [c] Melts with decomposition.

general formulas $[MSC_6H_4SM]_n$ (M = Cu(I) and Ag(I)) and $[MSC_6H_4S-]_n$ (M = Cu(II), Hg(II), Pb(II), and Ni(II)). For comparison, the properties of copper thiophenolate are also given.

Experimental Section

Physical Measurements. The infrared spectra of the complexes were obtained from KBr pellets, using a Beckman Model IR-33 for the 4000–600-cm^{-1} range and Perkin-Elmer Models 180 and 457 for the 600–300-cm^{-1} range. X-Ray powder patterns were obtained on a G.E. XRD-6 diffractometer with Cu Kα radiation and a crystal monochromator to eliminate the Cu Kβ line. The X-ray tube voltage was 45 kV; the amperage, 15 mA; the entrance slit, 1.0° medium resolution; and the exit slit, 0.2°. The proton magnetic resonance spectra were recorded on a TR-60 spectrometer. Solid-state absorption spectra of complexes wherever possible were obtained on KBr pellets using a Beckman Model DK-2A spectrophotometer.

Synthesis of 1,4-Dimercaptobenzene. The ligand 1,4-dimercaptobenzene was prepared *via* the reductive cleavage of 1,4-bis(ethylthio)benzene according to the method of Adams and Ferretti.[9] A solution of *p*-dibromobenzene in 2,4-lutidine was treated with the sodium salt of ethyl mercaptan and catalytic amounts of cuprous bromide to form the thioether.[10] The thioether was subsequently cleaved by sodium in liquid ammonia. The sodium salt of 1,4-dimercaptobenzene was isolated after evaporation of liquid ammonia. The free dithiol was obtained by treatment of the aqueous solution of the sodium salt with hydrochloric acid. The ligand was further purified by vacuum sublimation before use, mp 97.5–98.5°.

Preparation of Metal Complexes. In general the metal complexes were prepared by mixing under argon hot solutions of the appropriate metal compound (cupric chloride, cuprous chloride, mercuric chloride, silver acetate, lead acetate, and nickel tetracarbonyl) and dithiol in stoichiometric amounts. Argon was used to prevent the oxidation of dithiol in air. The complexes were filtered, washed successively with ethanol and ether, and dried *in vacuo* at 150–200°. The Cu(I) complex was also synthesized by heating an intimate mixture of freshly prepared cuprous chloride with excess dithiol under argon in the temperature range of 120–200°. The excess ligand was removed by vacuum sublimation at 200°. Copper thiophenolate was prepared by refluxing freshly prepared cuprous chloride and thiophenol in ethanol under a blanket of argon. The pale yellow solid was filtered and washed with boiling ethanol and benzene. The solid was dried *in vacuo* at 150°. The analytical data, colors, decomposition temperatures, and solvents used are given in Table I.

Reactions of 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) with Cu(I) Complexes of Thiophenol and 1,4-Dimercaptobenzene. In a typical reaction, a powdered mixture of $[CuSC_6H_5]_n$ and TCNQ in 1:1.5 mole ratio was charged into a Pyrex test tube and heated to 100° in an oil bath under a blanket of argon. After 4 hr, the white crystals which deposited on the colder parts of the test tube were carefully removed and identified as diphenyl disulfide, $C_6H_5SSC_6H_5$, mp 60–61°. The melting point reported for diphenyl disulfide is 61–62°.[11] The blue reaction mixture was then freed of unreacted TCNQ by vacuum-subliming the latter at 180–200°. The X-ray powder diffraction pattern of the blue-black solid left in the sublimation pot was in agreement with that of $Cu^+TCNQ\cdot^-$ prepared by the method of Melby, *et al.*[12] The interplanar spacings (*d* values in Å) were 7.96, 5.64, 5.04, 3.97, 3.53, and 3.11 for $Cu^+TCNQ\cdot^-$ obtained in this study and 7.96, 5.65, 5.05, 3.98, 3.53, and 3.12 for $Cu^+TCNQ\cdot^-$ prepared by the method of Melby, *et al.*[12] Similar reactions occurred when $[CuSC_6H_5]_n$ and TCNQ were suspended in benzene at room temperature or heated in sealed Pyrex tubes above 45° for several hours.

The Cu(I) complex of 1,4-dimercaptobenzene reacted similarly with TCNQ in a sealed Pyrex tube in the temperature range of 120–160°. The X-ray powder diffraction pattern of the reaction mixture revealed the presence of $Cu^+TCNQ\cdot^-$. It is reasonable to postulate that the other product was the polymeric sulfide, $-(SC_6H_4S-)_n$, which is known to be amorphous.[13] No further attempt was made to characterize the polymeric sulfide as it could not be separated from the reaction mixture.

Reactions of Metal Complexes with Organic Halides. A typical reaction was carried out by refluxing a sample of the mercaptide complex with excess organic halide (allyl bromide for the silver complex and methyl iodide for all other complexes) overnight. The insoluble solid residue in each case was filtered, washed with chloroform, and dried in air. The X-ray powder diffraction pattern of the residue showed that it was either AgBr or CuI depending whether the silver complex or the copper complexes reacted. The insoluble solid residue obtained from the reaction of Hg(II) complex with methyl iodide was purified twice from an *N,N*-dimethylformamide–methanol mixture. The very light yellow solid after drying melted at 145–145.5°. The proton chemical shifts (in deuterated dimethyl sulfoxide, τ relative to $(CH_3)_4Si$) were 2.32 (quartet due to aromatic protons, J = 20 Hz) and 7.10 (doublet due to methyl protons, J = 17 Hz) in the area ratio of 9:30, consistent with the dimethylsulfonium iodide salt of 1,4-bis(methylthio)benzene, $I(CH_3)_2SC_6H_4S(CH_3)_2I$. The residue obtained after evaporation of *N,N*-dimethylformamide and drying was shown to be HgI_2 by its X-ray powder diffraction pattern.

The filtrate after evaporation of the organic halide yielded a white solid when methyl iodide was used and an oil when allyl bromide was used to cleave the mercaptide complexes. The white solid after recrystallization from petroleum ether melted at 79–80°. The reported melting point for 1,4-bis(methylthio)benzene is 84–85°.[14] The proton chemical shifts (in $CDCl_3$, τ relative to $(CH_3)_4Si$) were 2.87 due to aromatic protons and 7.55 due to methyl protons. The area ratio of 1:1.54 is consistent with 1,4-bis(methylthio)benzene, $H_3CSC_6H_4SCH_3$. The oily residue obtained from the reaction of silver complex with allyl bromide was identified as 1,4-bis(allylthio)benzene, $H_2C{=}CHCH_2SC_6H_4SCH_2CH{=}CH_2$. The proton chemical shifts (in $CDCl_3$, τ relative to $(CH_3)_4Si$) were 2.87 (aromatic), 6.55 (doublet, $-CH_2-$), 4.18 (multiplet, $=CH-$), 4.90 (doublet, $=CH_2-$ trans to $=CH-$), and 5.12 ($=CH_2-$ cis to $=CH-$). The area ratios C_6H_4/$-CH_2-$/$-CH=$/$=CH_2$ were 1/1/0.6/1, consistent with 1,4-bis(allylthio)benzene.

Resistivity Measurements. Two-probe measurement of dc resistivities were made on compressed powder compacts pressed at 97,000 psi, employing brass electrodes in conjunction with a Keithley Model 600A electrometer for current measurements and a Keithley Model 160 Digital Multimeter for measurement of the voltage drop across the sample. Dc resistivities were taken as averages before and after reversing the applied potential (usually 1.5 V with a dry cell) to eliminate polarization effects. The electrical contact with the

Table II. Infrared Spectral Data of the Mercaptides (cm^{-1})^a

HSC_6H_4SH	2560 m, 1900 w, 1640 w, 1480 ms, 1400 ms, 1260 m, 1120 vs, 1020 s, 900 ms, 810 vs
$(CuS\text{-}C_6H_4SCu)_n$	1885 vw, 1625 w, 1560 m, 1470 vs, 1430 w, 1380 s, 1250 vw, 1175 vw, 1110 sh, 1092 vs, 1010 vs, 950 vw, 808 s, 535 m, 500 ms, 330 b, m
$(CuSC_6H_4S\text{-})_n$	1620 b, w, 1570 b, w, 1390 m, 1190 vw, 1110 s, 1015 s, 810 s, 495 vs, 535 sh
$(CuSC_6H_5)_n$	3060 m, 1920 b, w, 1890 vw, 1860 w, 1800 b, vw, 1620 w, 1590 vs, 1485 vs, 1450 m, 1380 vw, 1330 vw, 1310 w, 1270 w, 1190 vw, 1090 s, 1030 s, 1005 vw, 740 vs
$(PbSC_6H_4S\text{-})_n$	1480 vs, 1390 vs, 1260 vw, 1105 vs, 1015 s, 815 s
$(AgSC_6H_4SAg)_n$	1630 vw, 1475 vs, 1390 vs, 1350 vw, 1100 vs, 1010 s, 810 ms, 540 vs, 500 vs, 490 s
$(HgSC_6H_4S\text{-})_n$	1930 vw, 1620 b, w, 1580 vw, 1485 vs, 1400 s, 1110 vs, 1020 s, 830 ms, 540 s, 500 vs, 350 vs
$(NiSC_6H_4S\text{-})_n$	1900 b, w, 1620–70 b, 1570 m, 1475 vs, 1390 s, 1210 vw, 1180 w, 1090 b, m, 1015 m, 900 w, 810 m

[a] Key: b, broad; v, very; s, strong; m, medium; w, weak; sh, shoulder.

electrodes was made by G.E. Electronics Silver Print. The pellets were mounted between the electrodes and clamped in a small brass press described elsewhere.[15] The electrodes and the end plates of the brass press were insulated with ceramic material. The cell was suspended in a Pyrex vessel from a Teflon rod. The leads were brought out through individual tungsten Pyrex seals, and the electrical connections to external circuit were arranged through these seals. The conductivity vessel was placed in a dewar flask which served to keep the temperature constant. The cell was heated by an electrical tape wound around the Pyrex vessel. Temperatures in the vicinity of the sample were monitored by a chromel–alumel thermocouple attached to a potentiometer. Measurements were carried out *in vacuo* (10^{-4} Torr) and under argon atmosphere. Pellets were heated under vacuum to *ca.* 80° for 2–3 hr to remove any moisture or volatile matter occluded during pellet pressing and cooled to room temperature before measurements were made. The near-linear relationship between the applied voltage (12–50 V for Ag(I) and Cu(II) complexes and 1.5–6 V for Cu(I) complexes of thiophenol and 1,4-dimercaptobenzene) and the measured current indicates that the electrodes provided ohmic contact. No noticeable electrolysis was observed after prolonged passage of current, suggesting that the conductivity was electronic.

Results

Infrared Spectra. The infrared spectral data are given in Table II. The spectra of all complexes are similar and characterized by the occurrence of a single absorption near 810 cm^{-1} due to out-of-plane CH deformations of the aromatic ring, two absorptions near 1380 and 1460 cm^{-1} assigned to C=C skeletal in-plane vibrations, and two absorptions near 1010 and 1090 cm^{-1} attributed to C=S stretching vibrations.[16] A comparison with the spectrum of the free ligand revealed that these principal absorption bands in the spectra of the complexes are also the common features of the ligand. There was no evidence of a S–H vibration in the spectra of the complexes which for the free ligand is located at 2560 cm^{-1}. A slight shift to lower frequency of the principal absorption bands relative to the ligand was observed as a result of coordination of the metal to the ligand. A similar observation that the frequency of the strong dithiene bands does not change much with the metal was made previously by Schrauzer.[3a] Weak to strong absorptions were found in the spectra of Cu(I) and Hg(II) complexes in regions where M–S stretching bands are generally observed and are so assigned.[17] The remaining absorptions in the region 490–540 cm^{-1} are not readily assigned but are a common feature of all complexes. A band near 1580 cm^{-1} of weak to medium intensity, not found in the ligand spectrum, can be readily assigned to a conjugated aromatic ring.[16]

Table III. X-Ray Data for the Copper(I) Complexes of 1,4-Dimercaptobenzene and Thiophenol

Complex	*hkl*	I_{obsd}^{a}	d_{obsd}, Å	d_{calcd},^{b} Å
$[CuSC_6H_4SCu]_n$	100	80	10.53	10.49
	110	7	7.40	7.42
	200	7	5.24	5.24
	220	7	3.73	3.71
	300, 221	5	3.48	3.50
	310	4	3.30	3.32
	311	3	3.18	3.16
	400	4	2.61	2.62
	410, 322	4	2.54	2.54
$[C_6H_5SCu]_n$	100	>>100	12.31	12.20
	110	41	8.69	8.63
	210	26	5.44	5.55
	320	3	3.39	3.38
	420	4	2.73	2.73

[a] The observed intensities (I_{obsd}) are peak heights of the diffraction lines on a diffractometer tracing. [b] The calculated *d* spacings are based on a cubic unit cell with lattice constant $a = 10.49$ Å for $[CuSC_6H_4SCu]_n$ and 12.20 Å for $[C_6H_5SCu]_n$.

X-Ray Diffraction Data. According to X-ray powder diffraction, all M(I) ions form crystalline complexes. All M(II) complexes reported here are amorphous with the exception of the Hg(II) complex, which is crystalline. It is interesting that the X-ray powder diffraction pattern of any one complex regardless of the method of preparation remains unchanged with no significant variations in the lattice parameters. It is, therefore, possible that the crystalline mercaptide complexes prepared in this study are not linear high polymers, but are small discrete, possibly cyclic, molecules. A final solution to the structures of these mercaptides should await single-crystal X-ray structural determination. Thus far, we have been unable to prepare single crystals. The X-ray powder data for the Cu(I) mercaptides are given in Table III. As shown in the table, the data can be indexed based on a simple cubic unit cell. The density measurements indicate that there are four molecules in the unit cell of $[CuSC_6H_4SCu]_n$ and eight for $[C_6H_5SCu]_n$.

Physical Properties and Chemical Reactivity of the Metal Complexes. Good thermal stability and resistance to acids and bases marked each of the complexes prepared in this study. However, with the exception of the silver complex, concentrated nitric acid reacted vigorously with most mercaptide complexes. A common feature of all the complexes is their insolubility in common organic and inorganic solvents. This often is a consequence of the tendency of coordinated thiolo atoms to form bridges to adjacent metal atoms. All these properties suggest that the mercaptide complexes reported here should be coordination polymers involving sulfur bridges. Unfortunately, we were unable to determine the molecular weights because of the insoluble nature of these complexes. Contrary to previous experience with the reactions of S-bridged compounds, we found that several of these mercaptides were readily cleaved by organic halides under relatively mild conditions in accordance with reactions 1 and 2. Furthermore, the Cu–S

$$[\text{-}MC_6H_4S\text{-}]_n + RX \rightarrow MX_y + RSC_6H_4SR$$

$$(y = 2 \text{ for Mn(II) ions but 1 for Cu(II)}) \tag{1}$$

$$[MC_6H_4SM]_n + RX \rightarrow MX + RSC_6H_4SR \tag{2}$$

bonds were easily cleaved according to reactions 3 and 4 when

$$[C_6H_5SCu]_n + TCNQ \rightarrow Cu^+TCNQ\cdot^- + C_6H_5SSC_6H_5 \tag{3}$$

$$[CuSC_6H_4SCu]_n + 2TCNQ \rightarrow 2Cu^+TCNQ\cdot^- + [\text{-}SC_6H_4S\text{-}]_n \tag{4}$$

we attempted to incorporate 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) in the polymeric structure of Cu(I) complexes hoping to increase their electrical conductivity *via* the formation of charge transfer complexes. These reactions

Table IV. Electrical Resistivities of the Mercaptides

Entry	Complex	ρ_{25}, ohm cm	ρ_0, ohm cm	E_a,[a] ev
1	$[CuSC_6H_4SCu]_n$[b]	4.0×10	0.32	0.054
2	$[CuSC_6H_4SCu]_n$[b]	1.7×10^2	1.33	0.054
3	$[CuSC_6H_4S-]_n$	3.6×10^8	2.19	0.16
4	$[C_6H_5SCu]_n$[b]	5.1×10^4	3.39	0.11
5	$[AgSC_6H_4SAg]_n$	8.4×10^8	0.96	0.23
6	$[NiSC_6H_4S-]_n$	$\sim 10^9$		
7	$[HgSC_6H_4S-]_n$	$\sim 10^9$ (at 60°)		

[a] E_a defined by $\log \rho = \log \rho_0 + E_a/kT$. [b] Measured *in vacuo*. All others were measured under argon.

suggest that the formation of the charge-transfer complex precedes the breaking of Cu–S bonds. In one experiment, the green reaction product obtained on heating TCNQ and copper thiophenolate at 45° in a sealed Pyrex tube contained neither diphenyl disulfide nor $Cu^+TCNQ\cdot^-$. When exposed to air, it began to smell strongly of thiophenol. Presumably, the formation of the charge-transfer complex causes weakening of the Cu–S bond, which is then cleaved hydrolytically to form thiophenol or, in the absence of moisture, thermally to give diphenyl disulfide. This high reactivity of the mercaptide complexes toward electrophilic reagents such as organic halides and TCNQ indicates that the coordinated thiolo atoms still retain much of their nucleophilic character. The complexes of Cu(I), Cu(II), Pb(II), and Ni(II) appeared to catalyze the decomposition of hydrogen peroxide, but only the Cu(II) complex showed some catalytic activity in the decomposition of hydrazine.

Electrical Properties. The variation of the resistivity with temperature is displayed in Figure 1. Table IV shows values for ρ_0 (infinite temperature limit of the resistivity) and E_a (thermal activation energy for conduction), together with the resistivity at 25°. The results show a linear $\log \rho$ *vs.* $10^3/T$ relationship, consistent with a resistivity *vs.* temperature relationship of the form $\rho = \rho_0 e^{E_a/kT}$ for the activated conductivity, where E_a is the thermal activation energy for conduction. The activation energies determined from the slopes of the straight-line plots fall between 0.054 and 0.23 eV in the narrow temperature range of *ca.* 25–100° available to us. There is good consistency between the measurements made on samples from the same batch in all cases. For example, repeat measurements on analytically pure copper thiophenolate (entry 8 in Table I) and $(CuSC_6H_4SCu)_n$ (entry 3 in Table I) reproduced to within ±5%. The results, however, differed for samples of $(CuSC_6H_4SCu)_n$ prepared by different methods. Thus, the sample prepared by a solid-state reaction (entry 4 in Table I) had a resistivity of 170 ohm cm at room temperature as compared to 40 ohm cm for the analytically pure sample prepared in 2,4-lutidine (entry 3 in Table I). As the analytical data suggest, the higher resistivity in the former case is due to foreign impurities, possibly the polymeric sulfide, $[-SC_6H_4S-]_n$. As shown in Figure 1, the $\log \rho$ *vs.* $10^3/T$ straight-line plots for both samples are parallel and the thermal activation energy calculated from the observed slope is 0.054 eV in each case. This suggests that the conductivity is intrinsic to $[CuSC_6H_4SCu]_n$, and the higher resistivities of the impure samples are a result of the reduced mobilities of the charge carriers caused by the foreign impurity. For the most part the electrical resistivities of the M(II) complexes, including the Ag(I) complex, are very high and close to the range ascribed to insulators. Their resistivities are approximately of the same order of magnitude (~10^9 ohm cm) and seem to correlate with the intensity of the band near 1580 cm^{-1} in the infrared spectra, indicative of a conjugated aromatic ring and some degree of electron delocalization. The intensity of the 1580-cm^{-1} band is weakest for the Hg(II) complex, which also has the highest resistivity.

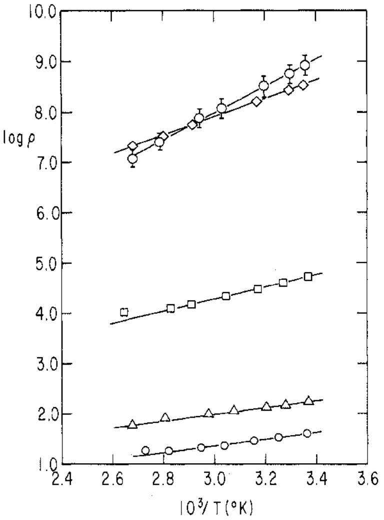
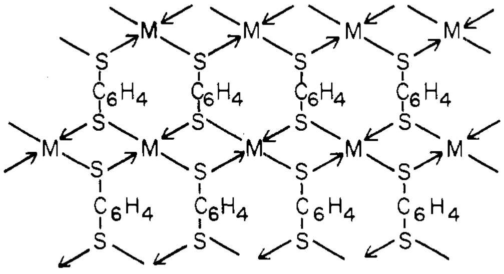


Figure 1. Temperature dependence of resistivity (ρ): ○, $[CuSC_6H_4SCu]_n$ (prepared in 2,4-lutidine); △, $[CuSC_6H_4SCu]_n$ (prepared by solid-state reaction); □, $[C_6H_5SCu]_n$; ⚲, $[AgSC_6H_4SAg]_n$; ◇, $[CuSC_6H_4S-]_n$.

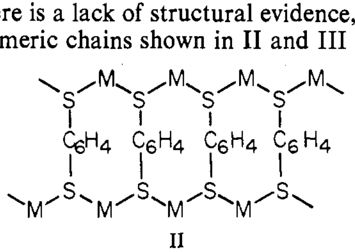
Discussion

In their general properties (good thermal and chemical stability and insolubility), the metal complexes of 1,4-dimercaptobenzene reported here closely resemble the mercaptide complexes of palladium(II) previously formulated as S-bridged high polymers of general formula $[Pd(SR)_2]_n$.[18] This formulation is generally accepted for other mercaptide complexes.[19–24] In view of the well-known tendency of the coordinated thiolo sulfur to form bridges and the overall similarity to the recently reported Pd(II) complexes of 1,2-ethanedithiol and 1,3-propanedithiol,[25] it would be reasonable to regard the metal complexes of 1,4-dimercaptobenzene of the type $-[MSC_6H_4S-]_n$ as coordination polymers with the aggregation shown in I.

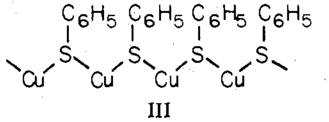


I

Similar polymeric structures involving sulfur-bridged metal chains are also postulated for metal complexes of the type $[MSC_6H_4SM]_n$ (M = Cu(I) and Ag(I)) and $[C_6H_5SCu]_n$. Although there is a lack of structural evidence, it is possible that the polymeric chains shown in II and III are arranged



II



III

in the solid state so as to allow the formation of metal–metal bonds which would enhance the ease of intermolecular electron transfer and hence carrier mobilities. The enormously high electrical conductivities of the Cu(I) complexes relative to the M(II) complexes would be in accord with this view. The high chemical reactivity of the complexes toward organic halides and the ready cleavage of the Cu–S bonds by TCNQ under very mild conditions appear to be consistent with a two-dimensional representation in which coordinated thiolo sulfur retains much of its nucleophilic character. It is possible that further cross linking could lead to a three-dimensional network. However, we believe that further cross linking would render the thiolo sulfur much less reactive toward organic halides. The facile cleavage of the metal mercaptides by organic halides is a reflection of the appreciable nucleophilic character of the coordinated thiolo sulfur and, therefore, tends to discount three-dimensional network structures for the complexes reported here.

The resistivities of compressed powder compacts of the mercaptide complexes in the temperature range of 25–100° fit the expression $\rho = \rho_0 e^{E_a/kT}$ for the activated conductivity. There was no apparent relationship between thermal activation energies for conduction and the band gap of the form $2E_a = E_g$, as required by the intrinsic band model. As the yellow color of many of these complexes would suggest, the conductivity may be extrinsic and impurity dominated. The impurity, however, need not be foreign and could arise from lattice imperfections. The solid-state absorption spectra of the copper complexes in KBr pellets in the range of 3125–14286 cm^{-1} showed continuous absorption extending into the visible region with onsets at much higher energies than the anticipated optical transition energies based on thermal activation energies for conduction. The onsets, which were neither sharp nor well defined, occurred at 5714 cm^{-1} (0.71 eV) for $[CuSC_6H_4SCu]_n$, 4098 cm^{-1} (0.51 eV) for $[C_6H_5SCu]_n$, and 3683 cm^{-1} (0.46 eV) for $[CuSC_6H_4S-]_n$. They do not correlate with the band gap calculated from the thermal activation energies for conduction.

The Cu(I) complexes of 1,4-dimercaptobenzene and of thiophenol are better conductors than those of Cu^{2+} and the other metals studied to date. It is interesting to note that both the electrical conductivities and the thermal activation energies for conduction are markedly influenced by the copper content of the mercaptide complexes. This is shown for the three copper complexes reported here. For example, the Cu(II) complex of composition $[CuSC_6H_4S-]_n$ (31.01 wt % Cu) has a resistivity of 3.6×10^8 ohm cm and $E_a = 0.16$ eV, whereas the Cu(I) complex of composition $[CuSC_6H_4SCu]_n$ (47.4 wt % Cu) has a resistivity of 40 ohm cm and $E_a = 0.054$ eV. The electrical resistivity (5.1×10^4 ohm cm) and the thermal activation energy ($E_a = 0.11$ eV) for $[CuSC_6H_5]_n$ (36.88 wt % Cu) fall between those of the Cu(I) and Cu(II) complexes of 1,4-dimercaptobenzene. This increase in the conductivity and decrease in the thermal activation energies for conduction with increasing copper content indicate that the conductivity mechanism may involve an interaction of copper 3d orbitals with the π^* orbitals of the ligand systems. However, the structural variations due to compositional differences should be even more important in influencing the electrical conductivities. As we pointed out earlier, the possible link-up of the polymeric chain structures of the Cu(I) complexes by the Cu–Cu bonds in the solid state would greatly facilitate intermolecular electron transfer. It is therefore likely that the formation of Cu–Cu bonds and the proposed d-orbital overlap, which will influence the probability of electron transfer *via* a tunneling process or the height of the activation energy barrier for electron hopping,[26] play important roles in determining the electrical conductivities of the copper complexes.

Finally, we mention that the metal mercaptides exhibit visible photoluminescence emissions at room temperature after excitation by 3650 Å: orange for $[AgSC_6H_4SAg]_n$, red for $[CuSC_6H_4SCu]_n$, purple for $[CuSC_6H_4S-]_n$ and $[HgSC_6H_4S-]_n$, and pink-red for $[C_6H_5SCu]_n$.

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Registry No. $[CuSC_6H_4S]_n$, 54325-84-7; $[CuSC_6H_4SCu]_n$, 54325-86-9; $[AgSC_6H_4SAg]_n$, 54325-88-1; $[HgSC_6H_4S]_n$, 54325-90-5; $[PbSC_6H_4S]_n$, 54325-92-7; $[C_6H_5SCu]_n$, 54325-93-8; $[NiSC_6H_4S]_n$, 54325-95-0; $Cu[SC_6H_4SCu]_3$, 54423-74-4; TCNQ, 1518-16-7; $I(CH_3)_2SC_6H_4S(CH_3)_2I$, 54325-82-5; 1,4-bis(allylthio)benzene, 24589-08-0; methyl iodide, 74-88-4; allyl bromide, 106-95-6.

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