Intrinsically Electrically Conducting Poly(metal tetrathiooxalates)

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ABSTRACT: Poly(metal tetrathiooxalates) (poly(MTTO)) have been synthesized and characterized. For M = Cu, Ni, and Pd and $\overline{DP}$ = 3–8, the compounds have a high absorption over a broad infrared frequency range and dc electrical conductivities of 1–20 $(\Omega\ cm)^{-1}$. Only the Cu and Ni compounds are studied in some detail because of their high conductivities. They have low negative values for thermoelectric power, indicating that the free carriers are negatively charged and highly mobile. Exposure to I_2 significantly reduces the conductivity, an effect that is partially reversible. These materials are intrinsic electronic conductors, requiring no doping, and their conductivities are not appreciably decreased upon exposure to ambient environment for several months. Temperature-dependent magnetic susceptibility measurements show appreciable Pauli susceptibility.

Introduction

Synthetic organic electronic conductors[1] have received much research attention. The interests intensified with the finding of synthetic organic conducting polymers. A brief introduction to the chemical nature of these systems is included to show the significance of the intrinsically conducting poly(metal tetrathiooxalates) (poly(MTTO)) discussed in this work.

Conventional metallic substances have partially filled conduction bands with a high density of states and electronic conductivity. The mobility of an electron is limited by scattering with other electrons. The extent of scattering decreases as the temperature decreases, with consequent increase of conductivity. Organic molecular compounds, on the other hand, are generally insulating because the energies separating filled and unfilled molecular orbitals are quite large. Extended delocalization of these orbitals tends to decrease this energy, leading to materials having band gaps that are small enough to allow thermal population of the conduction band yielding a semiconductor.

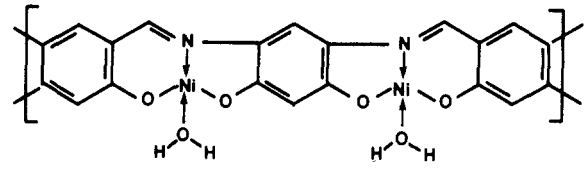
Unfilled bands can be created by virtue of partial charge transfer in organic donor–acceptor (DA) complexes as illustrated by $TTF^{0.54+}TCNQ^{0.54-}$ which has a conductivity,[2,3] σ, of 10^3 to 10^4 $(\Omega\ cm)^{-1}$. In these materials the conductivity is highest along the stacking axes of the DA complex, and the order of stacking is crucial. When the reduction potentials of the DA pair are too dissimilar, complete charge transfer takes place and the complex is insulating.[4]

Donor–acceptor complex polymers can have higher or lower conductivities than the monomeric DA complexes,[5,6] depending upon whether the polymer backbone facilitates or impedes the sandwich stacking. Metallic band structures can also be achieved through mixed valency as in the well-known case of poly(sulfur nitride), in which the sulfur atoms alternate between the formal +2 to +4 valence states.[7] Poly(sulfur nitride) exhibits metallic behavior,[8,9] and its conductivity can be enhanced by bromine doping.[10]

The electronic properties of poly(sulfur nitride) led researchers to the investigation of doped conjugated polymers as potential conductors. The prototype member of this family is poly(acetylene),[11] followed by poly(*p*-phenylene),[12] poly(*p*-phenylene sulfide),[13,14] poly(pyrrole),[15] poly(*p*-phenylenevinylene),[16] poly(phenylene oxide),[17] and poly(quinoline).[18] They all have filled valence bands and very low conductivities of from ca. 10^{-15} $(\Omega\ cm)^{-1}$ for poly(*p*-phenylene) and poly(*p*-phenylene sulfide) to ca. 10^{-5} for *trans*-poly(acetylene). They can be oxidized or reduced to form highly conducting materials. We have written a monograph on the various aspects of poly(acetylene)[19] and proposed a mechanism for the carrier-transport process.[20,21]

It would seem reasonable to expect the introduction of transition metal ions into a conjugated polymer chain to create a partially filled band and intrinsic conductivity. However, reported attempts have met mostly with disappointment. Undoped polymers containing ferrocene moieties, such as poly(ferrocenylene),[22] poly(ethynylferrocene), poly(ferrocenylenevinylenephenylenevinylene),[23] and poly(3-vinylbis(fulvalene)diiron)[24] are insulating. Oxidation can introduce carriers into these materials and they become semiconducting. The low conductivities observed may be attributed to the strong confinement of the charge to the ferricinium ion.[23,25]

Chelation of Ni(II) by the conjugated polymer 1[26] raised σ_{RT} from 5×10^{-13} $(\Omega\ cm)^{-1}$ for the polymer without the metal to 10^{-10} $(\Omega\ cm)^{-1}$. The polymeric Cu(II) complex of 1,5-diformyl-2,6-dihydroxynaphthalene dioxime[27] has a



(1)

higher σ_{RT} of 4×10^{-5} $(\Omega\ cm)^{-1}$ yet is still only semiconducting. The low carrier mobility may be partly attributable to weak $d\pi$–$p\pi$ interactions through N and O ligand atoms.

Morphology is an important factor for transport in conducting polymers. For instance, the conductivity of microcrystalline poly(sulfur nitride), synthesized by the reaction of $(Me)_3SiNSNSi(Me)_3$ and SCl_2,[28] is 5×10^{-2} $(\Omega\ cm)^{-1}$, while the σ_{RT} of solid-state polymerized single crystal is 5 orders of magnitude greater. Oriented continuous films of poly(*p*-phenylenevinylene)[29] have a σ_{RT} about 10^3 greater than that of samples of pressed powder.[16] In general, powdery preparations of conducting polymers have a σ_{RT} several orders of magnitude lower than samples with an ordered continuous morphology. In these cases, the thermoelectric power, $\mathcal{S}$, provides a more meaningful measure of intrinsic carrier transport because it is a zero-current measurement and interparticle resistance does not contribute to its value.

Transition-metal polymers utilizing conjugated bridging ligands have been investigated: the conducting properties of some of these are given in Table I. Both naphthalenetetrathiolate and tetrathiofulvalenetetrathiolate are tetrafunctional ligands that necessarily form undesirable

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Table I
Conductivities for Transition-Metal Type Polymers

	σ_{RT}, $(\Omega\ cm)^{-1}$		
metal	naphthalene-tetrathiolate[30]	tetrathio-fulvalene-tetrathiolate[31,32]	tetrathio-squarate[33]
Cu		10^{-1}	
Ni	10^{-7}	$10^{1.5}$	10^{-4}
Pd		10^{-3}	10^{-7}
Pt		10^{-2}	10^{-7}
Co	10^{-6}		
Fe		10^{-5}	

network products upon reaction with di- or trivalent metal ions. The Ni polymer of the latter ligand has a promising $\sigma_{RT} \sim 30\ (\Omega\ cm)^{-1}$; however, partial oxidation[32] is necessary for the polymer to attain this conductivity. Polymers of tetrathiosquarate, a difunctional ligand, with Ni(II), Pd(II), and Pt(II) with an approximate DP of 10–25 have been obtained, but their conductivities were disappointingly low. Recent investigations of transition-metal poly(benzodithiolenes)[34] have yielded materials having pressed-pellet conductivities that ranged from 10^{-4} to $2 \times 10^{-1}\ (\Omega\ cm)^{-1}$.

It is believed that strong $d\pi$–$p\pi$ interactions occur in the above metal-containing polymer systems as in the metal bis(dithiolenes).[35] Equivalent electronic structures may be obtained in polymers comprised of square planar divalent transition-metal ions and the tetrathiooxalate dianion (TTO). The TTO ligand can be synthesized by the electrochemical reduction of CS_2 in aprotic polar solvents. Careful investigation[36] showed that the initially formed TTO reacts with CS_2 further to produce mainly 2-thioxo-1,3-dithiole-4,5-dithiolate. The successful synthesis of TTO[37] involved its precipitation immediately upon formation at the electrode surface.

The main purposes of this work are the synthesis of poly(MTTO)s and studies of their magnetic and transport properties. The significance of this investigation is the demonstration that poly(MTTO)s are intrinsic electronic conductors. A brief description of preliminary results has been given previously.[38] Only the Cu and Ni compounds are studied in detail because of their high electrical conductivities.

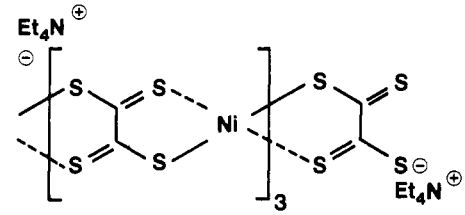
Experimental Section

Synthesis. Tetraethylammonium Tetrathiooxalate. TEATTO was synthesized by the procedure described by Jeroschewski.[37a] A 0.25 M electrolyte solution of Et_4NBr (Aldrich, Gold Label) in CH_3CN (Fisher, HPLC grade) was added to a large H cell and made 0.5 M in CS_2. A mercury pool cathode of ca. 50 cm^2 was used to reduce the CS_2 at −1.0 V vs. Ag/AgI and 5 °C. During electrolysis the solution turned red as an insoluble orange product formed. Continuous stirring kept this product suspended and prevented passivation of the Hg electrode surface.

The electrolysis was run at a high current of about 100 mA, which was limited by the cell resistance of about $10^3\ \Omega$ and potentiostat compliance voltage. During the synthesis the electrolyte in the counter electrode compartment was periodically replaced to prevent diffusion of Br_3^- through the porous frit. The precipitate was rinsed with cold CH_3CN and dried. In a typical experiment, 4.75 g of orange crystals could be obtained at a yield of 49% based on coulometry. The TEATTO was recrystallized from methanol, giving red platelets, mp 187–188 °C (lit.[37] mp 186–189 °C) with an overall yield of 26.6%. Elemental analysis and spectroscopic data for TEATTO were reported previously.[38] TEATTO is unstable in air; thus all subsequent reactions and handling were carried out under inert atmosphere.

Poly(NiTTO). A general procedure for the polymerizations of TEATTO with transition-metal ions is as follows. TEATTO (1 equiv) and a Teflon stir bar were introduced into a 200-mL pressure reactor under argon and then sealed with a butyl rubber liner and a crimped metal cap with two holes. Solvent, generally DMF or a DMF/methanol mixture, was added by cannula and stirred to dissolve the monomer at the desired temperature. A separate solution of the transition-metal salt was dissolved in the same solvent system and added to the TEATTO solution by cannula. Polymerization generally occurred rapidly but was allowed to proceed for up to 20 h to ensure complete reaction. The polymer was collected on a millipore filter, rinsed with methanol, and washed by successive additions of clean methanol. The product was then dried under vacuum.

The reaction of $Ni(OAc)_2 \cdot 4H_2O$ with TEATTO in methanol at 25 °C yields an insoluble black powder poly(NiTTO-a). In these reactions stoichiometric ratios of monomers were used to ensure that an imbalance would not limit the chain length. Elemental analysis results suggest that the structure of the product obtained is a TTO end-capped trimer. Four separate analyses were made, some after grinding to a fine powder, in different analytical laboratories. All samples showed C, H, N, and S content within experimental error. An average of the four analyses gave C, 27.16 (27.56); H, 3.76 (3.82); N, 2.55 (2.60); S, 49.02 (49.04); Ni, 17.51 by difference (16.9), where the values in parentheses are for structure **2**.[39]



(2)

In attempts to increase the solubility of the growing chains, reaction was also carried out under similar conditions but in the presence of 0.5 equiv of Bu_4NBr. It was hoped that the Bu_4N^+ ions would better solubilize the chain ends in the organic medium, preventing precipitation of short chains. Examination of the elemental analysis results for the product poly(NiTTO-b) indicate that the structure is again a TTO end-capped trimer with associated tetraalkylammonium ions: C, 32.62 (30.52); H, 4.89 (4.36); N, 2.70 (2.54); S, 42.98 (46.50); Ni, 17.6 (16.1). The values in parentheses represent a similar structure to **2** where the two Et_4N^+ chain ends are replaced by 1.5 Et_4N^+ and 0.5 Bu_4N^+ ions. This does not represent an exact structure but a close approximation.

Solubility tests showed products of both above polymerizations to be insoluble in most solvents except for slight solubility in polar aprotic solvents such as dimethylformamide (DMF). The polymers do not melt but slowly decompose when heated under vacuum. Thermogravimetric analysis (TGA thermogram) from 50 to 1000 °C at 20 °C min^{-1} under inert atmosphere shows a slow weight loss beginning at 100 °C which accelerates to reach 40% by 320 °C and eventually levels off at 78%. The weight of the residue corresponds to that predicted for a composition of NiS.

DMF was considered a logical choice as reaction solvent since the short-chain oligomers are slightly soluble in it. In practice, it was found necessary to use a DMF/methanol mixture to solubilize the TEATTO. Reactions have been carried out at 50 °C using both the acetate and nitrate salts of Ni(II) to give poly(NiTTO-c) and poly(NiTTO-d), respectively. It was thought that the nonchelating nitrate ion might allow the reaction of Ni(II) with TTO to proceed faster and longer chains might grow before precipitation occurred. Elemental analysis results for the nitrate reaction product suggest that a trimeric structure is still obtained: C, 23.30; H, 2.76; N, 2.82; S, 49.76.

The molecular weight of these organometallic chains might be controlled by three separate factors. The first, mentioned above, is stoichiometry. In a condensation polymerization an imbalance in reactive group concentration leads to a low molecular weight which is controlled by a modification of Carother's equation. Equivalent stoichiometry was used in all these reactions; thus imbalance is not limiting the molecular weight.

The second factor to consider in limiting the molecular weight of condensation type polymerizations is that the reaction is in equilibrium with an equilibrium constant that favors the reactants. In most condensation polymerizations this is usually overcome

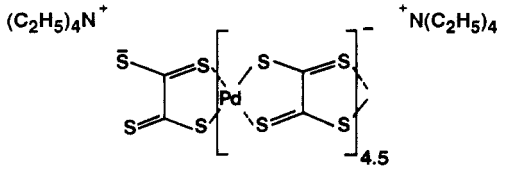
by removing the small-molecule side product (in this case a tetraethylammonium salt) as it forms, thus driving the reaction to high conversion and molecular weight. Though this was not expected for this type of chelating reaction, which forms strong Ni–S bonds, its possibility was examined. A reaction using nickel(II) nitrate was run in which the product was heated at 100 °C in distilled DMF to dissolve any Et_4NNO_3. After centrifugation, the solution was removed by cannula. This procedure, of heating in solvent followed by centrifugation, was repeated twice and then the poly(NiTTO-c) was washed as usual. If there were both Ni- and TTO-terminated chain ends, then they should have reacted to form higher molecular weight polymer with a decrease in the nitrogen content. Instead of observing this decrease, a small increase in nitrogen content was observed. This shows that the polymerization cannot be thermally driven. The increased nitrogen content may be due to some side reaction occurring with DMF at the elevated temperature. In a second reaction, run under the same conditions, the product was heated with additional metal ion. It was thought that if all the chains were TTO end capped then chain extension might occur, but no further reaction was observed.

These studies all suggest that solubility is the molecular weight limiting factor in these polymerizations. This would be expected if the chains are quite rigid.[39]

Poly(CuTTO). $Cu(OAc)_2 \cdot H_2O$ was polymerized with TEATTO using the DMF/methanol solvent system at 45 °C to give poly(CuTTO-a). Elemental analysis shows the chains to have an average $\overline{DP}$ of 4–5 and to contain both Et_4N^+ and OAc^- end groups, making a specific structure difficult to ascertain. The polymer is slightly soluble in most polar aprotic solvents but dissolves completely in hexamethylphosphoramide to give a deep blue solution. The polymer could not be precipitated by addition of nonsolvent.

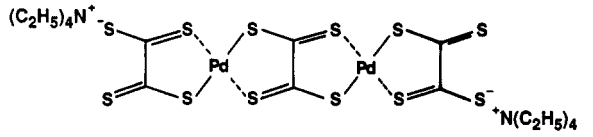
The effect of the anion associated with the transition-metal compound on these polymerizations was examined by using various Cu(II) salts. $Cu(SAL)_2$ (SAL, salicylaldehyde), $Cu(OAc)_2 \cdot H_2O$, and $Cu(NO_3)_2 \cdot H_2O$ were treated with TEATTO in DMF/methanol at 80 °C to give poly(CuTTO-b), poly(CuTTO-c), and poly(CuTTO-d), respectively. All of the reactions yielded insoluble black products that were filtered from the hot reaction mixtures and washed with methanol. An approximate $\overline{DP}$ can be determined from the elemental analysis results assuming that most of the chains are end capped with TTO ligands and their associated Et_4N^+ ions. A $\overline{DP}$ of almost 8 is seen when the nonchelating nitrate ion is used and this falls to a $\overline{DP}$ of 2.6 for the strongly chelating salicylaldehyde ligand. Thus a less strongly complexed metal ion gives a longer chain before precipitation occurs.

Poly(PdTTO). The initial reaction between TEATTO and $PdCl_2$ to form poly(PdTTO-a) was carried out in a DMF/methanol mixture at 80 °C. The black insoluble product was isolated by hot filtration and washed thoroughly with methanol. As seen with the NiTTO and CuTTO polymers, the powder did not melt but decomposed slowly between 150 and 200 °C under vacuum. It was only slightly soluble in polar aprotic solvents such as DMF or tetramethylene sulfone. Elemental analysis shows that the polymer has an average $\overline{DP}$ of 4.5 and is end capped with TTO as shown in the postulated structure **3**:[39] C, 19.78 (20.54); H, 2.41 (2.54); N, 1.88 (1.77); S, 43.64 (44.63); Cl, <0.2 (0.0).



(3)

Most of the polymerizations discussed so far have employed DMF in the reaction mixture. The conclusion that the materials formed are actually low molecular weight oligomers is based heavily on the elemental analysis results, especially the nitrogen content. To verify that the nitrogen could not be attributed to the reaction of the chain end with DMF, the synthesis of poly(PdTTO-b) was carried out with tetramethylene sulfone as the solvent. It was found that $PdCl_2$ is only slightly soluble in tetramethylene sulfone. The reaction was carried out by stirring the dissolved TEATTO with the $PdCl_2$ dispersion at 80 °C for 20 h, in which time the reaction was complete. A very small amount of insoluble material (ca. 16 mg) was discarded, and the product was precipitated with methanol. A good yield of black powder was obtained, washed with methanol, and dried. Elemental analysis shows the product to be a TTO end-capped dimer as shown in the proposed structure **4**:[39] C, 29.89 (23.39); H, 4.41 (4.30); N, 3.01 (3.01); S, 40.29 (41.29); Cl, <0.1 (0.0).



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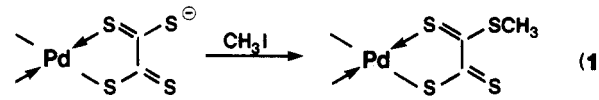
Poly(PdTTO-b) could be easily redissolved in tetramethylene sulfone, which is important to the consideration of these materials for further reactions. These oligomers might be used for block copolymers in which flexible spacers may be inserted between the rigid conducting domains.

The feasibility of this was shown by reaction of poly(PdTTO-b) with excess CH_3I in sulfolane at 40 °C and subsequent precipitation by methanol. A black powder was collected, having an analysis of C, 15.50; H, 1.31; N, 0.34. The theoretical values for $H_3CS_4C_2(PdC_2S_4)_2CH_3$ are C, 13.70; H, 0.896; N, 0.0. The decrease in N content from an original value of 3.01% suggests that 90% of the thiolate chain ends were methylated as shown in eq 1.[39]



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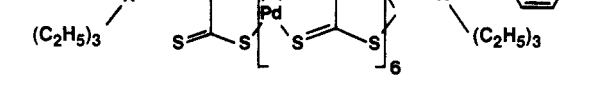
Since solubility is the controlling factor for the final chain length of these metal tetrathiooxalates, a method of keeping the growing chains in solution longer was desired. The effect of exchanging the Et_4N^+ with an ion more soluble in the reaction medium was explored. Benzyltriethylammonium chloride (BTEAC) was chosen as a potential phase-transfer reagent for this case. Poly(PdTTO) was synthesized by reacting TEATTO with $PdCl_2$ in the presence of 2 equiv of BTEAC. The reaction was carried out in DMF at 85 °C for 15 h. The BTEAC was able to effect the dissolution of TEATTO with no methanol. Two fractions were isolated.

The first fraction, poly(PdTTO-c), was insoluble in the hot reaction medium and was collected by hot filtration, methanol washed, and dried. Elemental analysis comparison of the Pd to N content indicates a $\overline{DP}$ of 6.2. The structure can be modeled by a TTO end-capped hexamer having mainly $BTEA^+$ ions associated with it as shown in the postulated structure **5**:[39] C, 25.46 (22.97); H, 2.30 (2.10); N, 1.35 (1.34); S, 39.04 (42.87). This



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material was insoluble in DMF and sulfolane. Therefore, the concept of solubilizing the chain ends was only moderately successful, resulting in slight increase of MW. The second fraction, poly(PdTTO-d), was soluble in the reaction medium and was collected by precipitation and washing with methanol. The elemental analysis was complicated by the presence of 0.67% chlorine, probably as Pd–Cl end groups. Thus simple oligomeric structure could not be rationalized. If the Pd–Cl is present as end groups, it is not understood why they did not react with the more abundant TTO end groups in solution. An approximate $\overline{DP}$ of 4–5 could be estimated for this sample having mainly TTO and associated $BTEA^+$ chain ends.

Poly(PtTTO). The Pt(II) analogue of these tetrathiooxalate complexes was synthesized with K_2PtCl_4 dissolved in DMF with

the assistance of 2 mol equiv of 18-crown-6. TEATTO was dissolved in DMF/methanol and the two solutions reacted for 8 h at 80 °C. In all of the polymerizations discussed so far, in which an insoluble product formed, precipitation occurred at a very fast rate. This was not so in the case of the $PtCl_4^{2-}$ ion. Instead, the black insoluble product formed slowly, leaving a pink solution. We attribute this to the slow displacement of four Cl^- ions per metal atom, while previous reactions required the displacement of two more labile ligands. The poly(PtTTO-a) was isolated by hot filtration, washed thoroughly with methanol, and dried. Elemental analysis results are complicated by the presence of both Cl and Et_4N^+ but show a S/Pt of 3.9 and an approximate $\overline{DP}$ of 4.

Poly(CoTTO). In examining this series of compounds, we found the effect of a metal ion that would not easily attain a square planar geometry to be of interest. Co(II) was chosen for its d^7 electron configuration to complement the d^8 Ni(II) and d^9 Cu(II), and its previous utility in metal bis(dithiolene) complexes.[41] It is known that Co(II) complexes can coordinate bis(dithiolene) ligands in a planar geometry but also dimerize to form axial Co–S bonds. This stabilization through dimerization leads to square-pyramidal coordination about the metal atom.

Poly(CoTTO-a) was synthesized by treating TEATTO with $Co(NO_3)_2 \cdot 6H_2O$ in a DMF/methanol mixture at 80 °C and was collected by hot filtration. The product was washed with methanol and dried to a black powder. Elemental analysis shows the material to be composed mainly of dimers and trimers.

Transport Properties. Conductivity. Electrical conductivity, σ_{RT}, measurements were made by the four-probe technique. Powders were pressed into disks at ca. 15 000 psi, which were subsequently cleaved to the desired dimensions with a razor blade. Contacts were made with Pt wire and Electrodag 502 (Acheson Colloids). A four-probe press cell was developed for materials having a high conductivity but little physical integrity in pellet form. Glass-filled Teflon rings and plungers prevented any metal from contacting the sample except for the four thin contacts.

Temperature dependence of conductivity was measured from −190 to +25 °C using a Heli-Tran Cryogenic System (Air Products) or by immersion of a glass four-probe apparatus,[42] filled with 0.5 atm of N_2 or He, in a series of solvent slush baths.

Thermoelectric Power. $\mathcal{S}$ was measured on the pressed pellets using a device described previously.[43] The pellet was clamped on two copper blocks that were maintained at a 5–10 °C difference in temperature. The resulting potential difference was measured. Charge polarization experiments were carried out with a PAR 173 potentiostat and 179 coulometer.

Magnetic Properties. EPR. EPR spectra were recorded at −196 °C on a Varian E-9 X-band spectrometer. DPPH was used as a g-value reference in the dual cavity. Samples of 1–20 mg were prepared by weighing in capillary tubes and sealing under vacuum in quartz sample tubes. Spin concentrations were determined by comparison of the integrated signal intensity to standard solutions of tetramethylpiperidinoxyl in hexadecane.

Magnetic Susceptibility. Magnetic susceptibility, χ_m, was measured with a SHE Model VTS magnetometer/susceptometer over a wide range of temperature. The system can detect a change in volume susceptibility of only 10^{-11} emu/cm.

Results and Discussion

Transport Properties. The σ_{RT} and $\mathcal{S}$ of poly(MTTO) are summarized in Table II. All the compounds are electronic conductors; typically passage of 5–6 C through ca. 5 mg of sample resulted in no change in its resistance.

The thermoelectric power is a superior measure of carrier transport not only because it is not complicated by interparticle resistance[43] but also because its sign corresponds to the charge of the carrier. Therefore, small negative values of $\mathcal{S}$ indicate conductors with electrons as majority carriers, whereas conducting substances with positively charged carriers have small positive values of $\mathcal{S}$. Semiconductors have large values of $\mathcal{S}$ and positive or negative sign for p- or n-type, respectively.

The $\mathcal{S} = -20\ \mu V\ K^{-1}$ value for poly(NiTTO) shows that the substance is an electronic conductor with high carrier mobility. This is supported by lack of transmission over the broad infrared frequencies due to absorption and reflection by free carriers. The σ_{RT} is up to 20 $(\Omega\ cm)^{-1}$ for pressed pellets and may be expected to be greater when ordered continuous specimens are available.

Table II
Transport Properties of Poly(metal thiooxalates)

sample	$\overline{DP}$	$\mathcal{S}$, $\mu V\ K^{-1}$	σ_{RT}, $(\Omega\ cm)^{-1}$
poly(NiTTO-a)	3		4
poly(NiTTO-d,e)	3	−20	20
poly(CuTTO-a)	4–6		0.4
poly(CuTTO-b)	2.6	−130	0.06
poly(CuTTO-c)	4.6	−10	0.6
poly(CuTTO-d)	7.8	−12	3.0
poly(PdTTO-a)	4.5	−50	1.0
poly(PdTTO-b)	2	<−10	0.02
poly(PdTTO-c)	6.2	−50	0.23
poly(PdTTO-d)	4–5	<−10	6×10^{-4}
poly(PtTTO)	4	+10	0.4
poly(CoTTO)	2–3	−4500	10^{-3} to 10^{-4}

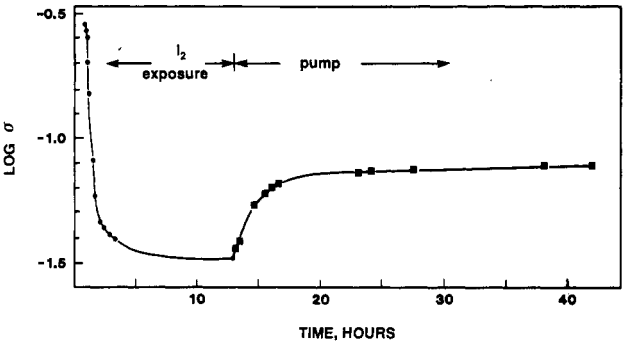

Figure 1. Effect of iodine oxidation on the dc conductivity of poly(CuTTO-a).

Poly(CuTTO-a,c,d) are also metallic conductors with negatively charged carriers. The value of $\mathcal{S}$ is larger for poly(CuTTO-b), which may be due to the low $\overline{DP}$ of ca. 2.6 or attributed to end-group effects. Poly(CuTTO)s are amorphous as evidenced by the lack of reflections seen by X-ray diffraction; infrared spectroscopy also shows only a broad featureless absorption.

Ribas and Cassoux[32] stressed that obtaining polymers of nickel(II) tetrathiofulvalenetetrathiolate that have high conductivity requires oxidation. Polymers they synthesized under inert atmosphere only exhibited a $\sigma_{RT} \sim 10^{-4}$ $(\Omega\ cm)^{-1}$. We have studied the effect of oxidation by I_2 on σ_{RT} for poly(CuTTO). A pressed-pellet sample of poly(CuTTO-a) was exposed to I_2 vapor in an evacuated glass vessel and its conductivity monitored. Figure 1 shows a rapid decrease in conductivity, with I_2 doping, that stabilizes at a value corresponding to a ca. 1 order of magnitude drop after 13 h. The reaction is at least partially reversible since pumping on the sample removed I_2 and the conductivity increased. Cracks that formed in the sample may have prevented the conductivity from returning to its original value. The same behavior was also observed for poly(NiTTO) (Figure 2). These experiments showed that oxidation of poly(CuTTO) and poly(NiTTO) by I_2 tends to reduce the electron carrier concentration and σ_{RT}. However, this charge-transfer interaction is weak, as evidenced by partial recovery of σ_{RT} upon removal of I_2.

Poly(CuTTO-c) and poly(CuTTO-d) have nearly the same $\mathcal{S}$ values; however, the σ_{RT} of pressed pellets differ by a factor of 5. Similar differences were seen between poly(NiTTO-a) and poly(NiTTO-d,e), even though the samples have the same $\overline{DP}$. Small morphological differences in the pressed pellets may cause these discrepancies in σ_{RT}.

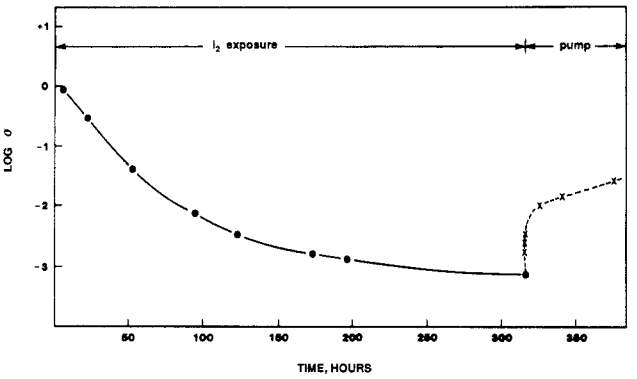

Figure 2. Effect of iodine oxidation on the σ_{RT} of poly(NiTTO-a).

That σ_{RT} is not a reliable measure for intrinsic carrier mobility is demonstrated strikingly by the poly(PdTTO). Samples a and c have $\mathcal{S} = -50\ \mu V\ K^{-1}$ and $\sigma_{RT} \sim 0.2$–$1.0\ (\Omega\ cm)^{-1}$. On the other hand, samples b and d have $\mathcal{S} < -10\ \mu V\ K^{-1}$. This indicates higher intrinsic carrier mobilities for the latter samples than for samples a and c; instead the σ_{RT} values are 2–3 orders of magnitude smaller for the compounds with smaller thermoelectric power values.

Of considerable interest is the possible dependence of $\mathcal{S}$ on $\overline{DP}$. Our data reveal no simple relationship. For poly(CuTTO), the magnitude of $\mathcal{S}$ decreases as $\overline{DP}$ increases from 2.6 to 4.6; however a further increase of $\overline{DP}$ to 7.8 causes no change in $\mathcal{S}$. In the case of poly(PdTTO), no relationship is apparent. Samples a and d have approximately the same $\overline{DP}$ but exhibit different $\mathcal{S}$ values.

Poly(PtTTO) has $\mathcal{S} = +10\ \mu V\ K^{-1}$. Therefore the charge carriers are holes. The positive sign for $\mathcal{S}$ has been repeatedly measured and confirmed. Oxidation of poly(PtTTO) may have occurred during the polymerization, though a reason for this is not obvious. The substance should have a singlet ground state. Therefore the p-type conduction may be due to an impurity ion or to mixed valency.[44]

The only transition-metal TTO polymer studied in this work that is not highly conducting is that obtained from Co(II). The substance is an n-type semiconductor with $\mathcal{S} = -4500\ \mu V\ K^{-1}$ and a corresponding low σ_{RT}. Co(II) is easily oxidized to Co(III), which has no unpaired spins for strong ligand field complexes. If some oxidation occurred during the synthesis of poly(CoTTO), then the carrier concentration would be significantly decreased. Furthermore, compounds of octahedral Co(III) would be nonplanar, which should reduce the through-metal π interactions of the TTO system.

Air Stability of Conductivity. We have studied the stability of conductivities of the poly(MTTO)s in air and the results are shown in Figure 3. There was no change of σ_{RT} of poly(PdTTO) and poly(PtTTO) for up to 2 mo. The conductivity of poly(NiTTO) and poly(CuTTO) decreases by less than an order of magnitude over this same period. These decreases are much smaller than those found for most doped conducting polymers. The small decrease of conductivity for the poly(NiTTO) is accompanied by changes in its elemental analysis from C (27.16), H (2.79), N (2.53), and S (48.16) for a fresh specimen to C (25.19), H (3.74), N (2.42), and S (43.80) after 1 mo of aging in air, which indicates a possible slow oxidation and moisture absorption.

Poly(CoTTO) is not air stable and loses more than 3 orders of magnitude in conductivity in 3 weeks of exposure to air. This is consistent with the postulated oxidative instability of this polymer discussed above.

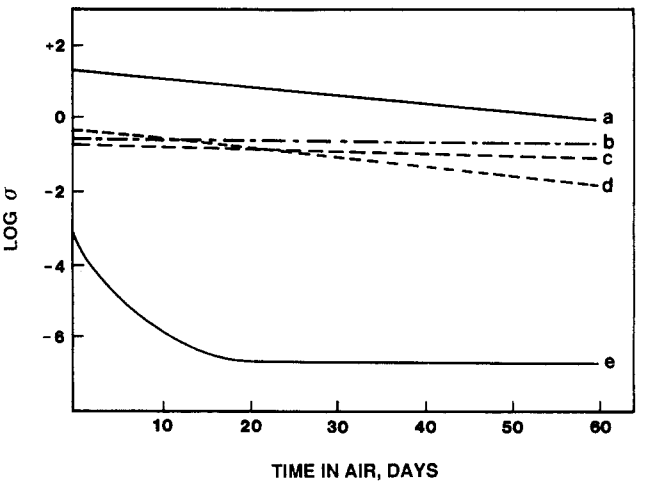

Figure 3. Air stability of conductivity: (a) poly(NiTTO); (b) poly(PdTTO); (c) poly(PtTTO); (d) poly(CuTTO); (e) poly(CoTTO).

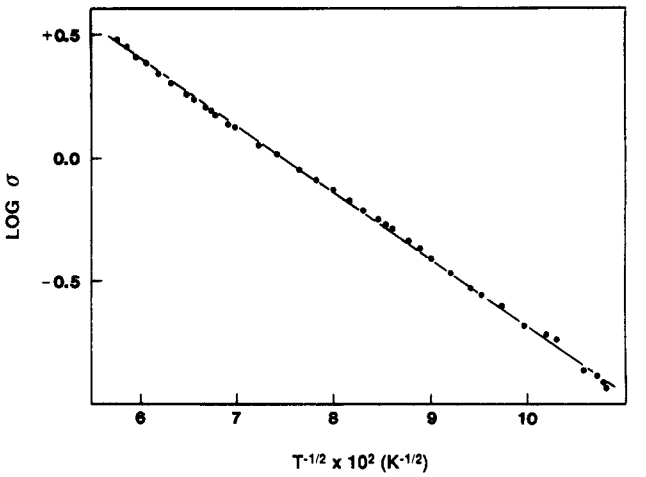

Figure 4. Log conductivity vs. $T^{-1/2}$ for poly(CuTTO-d).

Temperature Dependence of Conductivity. The temperature dependence of conductivity has often been used to deduce the mechanism of conduction for conducting polymers (see discussion in ref 19), but this practice has many shortcomings.[21]

The variation of conductivity with temperature has been measured for poly(CuTTO-d). The results give a nonlinear Arrhenius plot; between −187 and −50 °C, $E_a \sim 0.031$ eV at low temperatures, which increases to 0.055 eV between −50 °C and room temperature. The same data is linear for the log σ vs. $T^{1/2}$ plot (Figure 4). The temperature dependence for poly(NiTTO) is linear for log σ vs. T^{-1} over the temperature region −150 to +25 °C with an activation energy of about 0.02 eV. The data also give a linear log σ vs. $T^{1/2}$ plot. These ambiguities are also found to be true for doped poly(acetylenes).[21]

Magnetic Properties. The magnetic susceptibility of poly(NiTTO) was measured from 4.5 to 100 K. The data are plotted in Figure 5 both as χ_m^{-1} vs. T and $\chi_m T$ vs. T. Very interesting studies have been made on bimetallic dithiooxalate compounds.[40] The $[PdMn(DTO)_2]_x$ compound exhibits a Curie–Weiss behavior; i.e., the χ_m^{-1} vs. T plot is linear according to $\chi_m^{-1} = C/(T - \Theta)$ with the Curie constant $C = 4.39$ mol cm^3 K and the Curie–Weiss temperature $\Theta = -1.8$ K. The susceptibility data for the $[CuMn(DTO)_2]_x$ are more complicated. The plot of $\chi_m T$ vs. T is constant for Curie susceptibility at high temperatures. There is a minimum of $\chi_m T$ at 130 K, which is

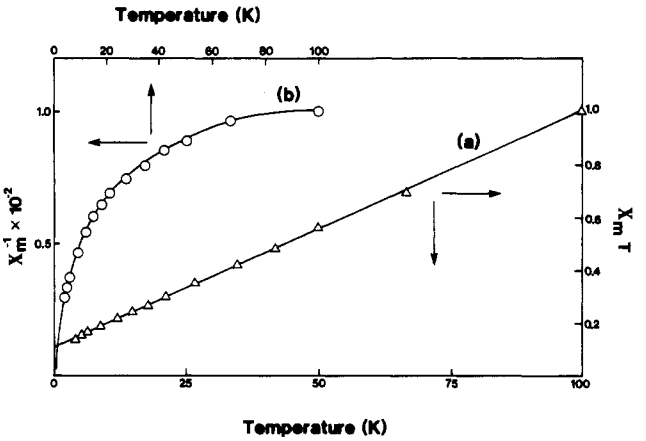

Figure 5. Magnetic susceptibility data for poly(NiTTO): (a) $\chi_m T$ vs. T; (b) χ_m^{-1} vs. T.

Table III
Summary of EPR Characteristics for Metal Tetrathiooxalate Complexes

sample	g value	linewidth, G	metal atoms per spin
PdTTO-1	2.00	60	160
CuTTO-4	2.00	150	30
PtTTO-1	2.02	140	95
NiTTO-4	2.02, 3.96	100/100	
CoTTO-1	2.01, 5.68	50/1200	

attributed to a short-range ordered antiferromagnetic state where the copper spins are antiparallel to the manganese spins. $\chi_m T$ increases sharply between 130 and 7.5 K. The explanation given[40] is that the correlation length in the one-dimensional chain increases, which leads to a ferrimagnetic short-range order. At temperatures between 7.5 and 4.2 K, $\chi_m T$ decreases due to interchain antiferromagnetic coupling.

The χ_m^{-1} vs. T plot for poly(NiTTO) shows it does not obey a simple Curie–Weiss relationship. On the other hand, the $\chi_m T$ vs. T plot is strikingly linear over the entire temperature range of 4.5–100 K. This is consistent with

$$\chi_m^{tot} = (C/T) + \chi^{core} + \chi^{Pauli} \quad (2)$$

where χ^{core} is the diamagnetic susceptibilities, which are much smaller than the Pauli susceptibility χ^{Pauli}. From the slope of Figure 5a we estimated $\chi^{Pauli} \sim 9 \times 10^{-3}$ emu mol^{-1}. The intercept should correspond to the Curie constant, but the intercept is 0.1 emu K mol^{-1}, which is about one-third as large.

Figure 5b suggests that antiferromagnetic exchange interactions are probably also present in poly(NiTTO) as in the bimetallic DTO complexes. However, there is no maximum in the plot; if χ_m^{-1} begins to decrease for $T >$ 100 K then $-2J/k > 100$ K, where J is the $J\bar{S}_1 \cdot \bar{S}_2$ coupling constant.

All the poly(MTTO) samples that have been studied exhibit EPR signals at −196 °C. This includes all of the transition-metal ions that have been discussed above: Ni, Pd, Pt, Cu, and Co. None of the samples have detectable EPR signals at room temperature.

The spectra of the Cu, Pd, and Pt complexes are similar to one another; representative spectra are shown in Figure 6. Spectra for the Ni and Co complexes are shown in Figure 7. A summary of the EPR characteristics for these samples is given in Table III. It can be seen that all of the samples exhibit a signal at a g value of 2.0 and these have linewidths of 50–150 G. This is significant considering the varied d electron configurations of the metal ions employed. The behavior is indicative of strong $d\pi$–$p\pi$ interactions with the ligand. The spin concentrations are much less than one spin per metal atom or repeat unit. This is expected for magnetic exchange between most of the metal ions.

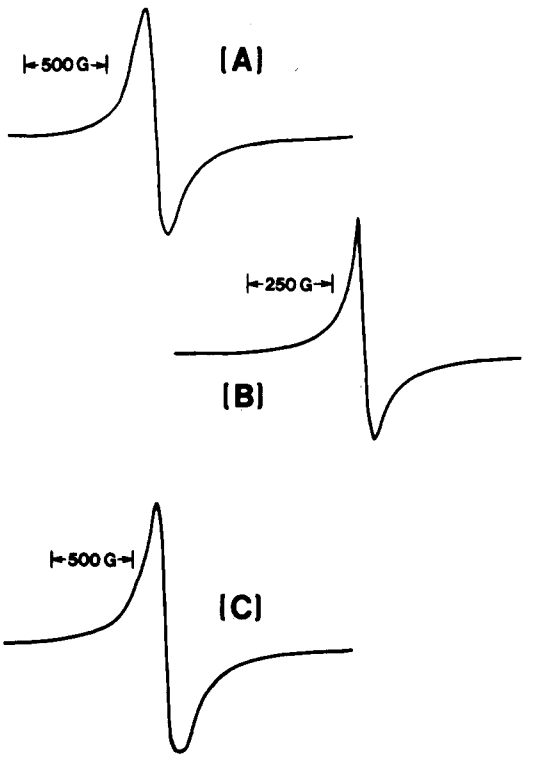

Figure 6. Representative EPR spectra for (a) poly(CuTTO); (b) poly(PdTTO); (c) poly(PtTTO).

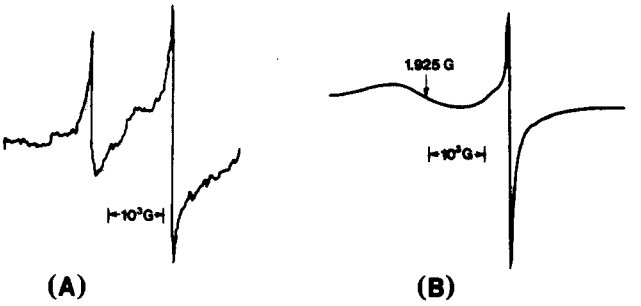

Figure 7. Representative EPR spectra for (a) poly(NiTTO); (b) poly(CoTTO).

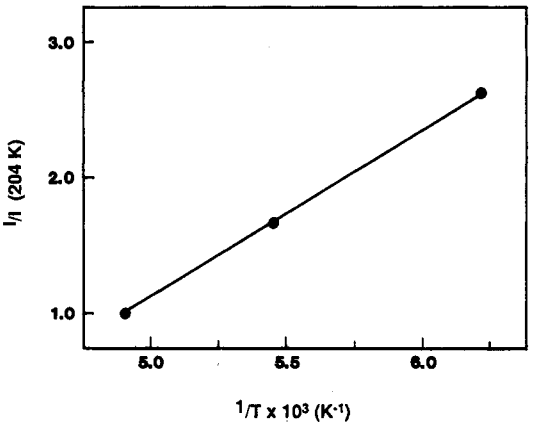

Figure 8. Temperature dependence of the EPR intensity for poly(PdTTO).

A study of the temperature dependence of the EPR intensity was carried out between −70 and −100 °C on poly(PdTTO-a). Figure 8 shows that the signal is strongly Curie dependent in this range, which explains the disap-

pearance of the EPR at room temperature.

The EPR of the Ni complex contains a resonance at half-field. This means that those noninteracting nickel ions have a d^8 triplet ground state. A microwave saturation study shows both the $g = 2$ and the half-field signals increase in intensity with the square root of microwave power. The EPR of poly(CoTTO) is characteristic for a high-spin Co(II) in low-symmetry field.

Conclusions

A series of transition-metal tetrathiooxalate compounds have been synthesized with the goal of forming intrinsically conducting, linear, polymer systems. These complexes are actually oligomers with $\overline{DP}$ of 3–8. However, the results are not less significant because of the low $\overline{DP}$. We have synthesized poly(acetylenes) with $\overline{DP}$ of 15–16 000 ($\bar{M}_n$ = 400–900 000)[46] and found they have comparable undoped and doped conductivities.[21,47] Therefore, we expect no great improvement of electrical conductivity for only higher MW poly(MTTO). If on the other hand poly(MTTO)s with large values of $\overline{DP}$ can be cast into continuous films with physical integrity and mechanical strength, then metallike intrinsically electrically conducting polymers may be realized. The Ni, Cu, and Pd derivatives are particularly interesting. They all have high electronic conductivities and low negative thermoelectric power without doping. The carriers are electrons as indicated by $\mathcal{S} < 0$ and the fact that oxidants such as iodine decrease their conductivities. These substances are distinct from the various transition-metal-containing polymers mentioned above, which all require doping except for the Fe polymer.[34]

The Ni, Cu, Pd, and Pt TTO polymers are relatively stable in air and ambient environment. Among conducting organics only the oxidized polyheterocycles may have comparable stability. It is encouraging that systems have been obtained that do not require the stringent handling procedures necessary for so many other conducting polymers.

The poly(MTTO)s are conducting because their highest occupied molecular orbitals derived from the $d\pi$ orbitals of the metal ion and the $p\pi$ ligand orbitals of TTO are only partially filled. Long-range order of the metal and/or ligand is not essential for carrier transport; the compounds are not crystalline according to X-ray diffraction.

One feels the necessity of commenting on the mechanism of carrier transport for such a new system. This is usually based on the certain predicted $\sigma(T)$ relationship for a particular mechanism. However, more than one mechanism can share the same $\sigma(T)$ dependency and often times data covering a limited temperature range can be fitted with several different functional forms of $\sigma(T)$.[21] Finally, $\sigma(T)$ data on specimens pressed from particulate materials are questionable for detailed analysis of temperature dependency. Recently, voltage-shorted compaction measurements on doped poly(acetylenes)[48,49] showed an actual increase of conductivity with decreasing temperature; the $\sigma \propto T^{-2}$ metallic conductivity is like those found in charge-transfer salts.[49,50] With these qualifications in mind, we speculate on the possible conduction mechanism for poly(MTTO)s. The observed $\sigma(T^{1/2})$ dependence (Figure 4) suggests either 1-D variable-range hopping or fluctuation-induced tunneling for small volume fraction of metallic islands.[19] The fact that poly(NiTTO) exhibits a significant χ^{Pauli} tends to favor the latter mechanism for conduction.

Acknowledgment. We thank Bernard Wasserman of the Massachusetts Institute of Technology for performing the magnetic susceptibility measurements. This work was supported in part by a grant from NSF.

References and Notes

(1) Abbreviations: TTF, tetrathiafulvalene; TCNQ, tetracyanoquinodimethane; TMTSF, tetramethyltetraselenafulvalene; X^-, univalent anion; BEDTTTF, bis(ethylenedithiotetrathiafulvalene); $[SN]_x$, polythiazyl; σ_{RT}, room temperature dc conductivity; MW, molecular weight; $\overline{DP}$, degree of polymerization; TTO, tetrathiooxalate dianion; poly(MTTO), poly(transition metal tetrathiooxalates); TEATTO, tetraethylammonium tetrathiooxalate; DTO, dithiooxalate.
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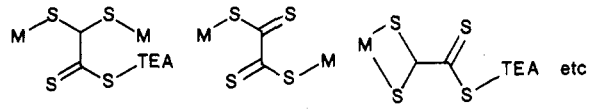
(39) The poly(MTO)s are difficult to characterize because of their insolubility and infusability. They are also not easy to analyze. There are no hydrogens for NMR and only one type of carbon. Analysis of sulfur and metals are performed both at the Microanalytical Laboratory of the University of Massachusetts and by Galbraith for confirmation. The errors of their analysis are generally greater than considered acceptable for C and H. A referee objected to the structures postulated for the poly(MTO)s. However, the X-ray structures have been obtained[40] for the related bimetallic catena μ-dithiooxalates compounds $AMn(S_2C_2O_2)_2(H_2O)\cdot 4.5H_2O$ (A = Cu, Ni, Pd, Pt). Our proposed structures are the same as these. The referee suggested the following alternative structures:



They seem improbable because of their low coordinate states.
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(44) A referee pointed out that in the polymers containing Cu, Ni, and Pd there may exist a small amount of metal in the +1 oxidation state. Now conduction could occur via intermolecular redox reactions between M^{1+} and M^{2+}, i.e., mixed-valence states. The n-type conductivity can be explained when M^{2+} is in excess; the M^{1+} is electron excessive in a "sea" of M^{2+} and hence an n carrier moves.[45] Just the reverse would be true for an excess of M^{1+} for p-type conductivity. The former may be an explanation for the n-type conductivity for poly(PtTTO), though Pt^{1+} is not a common oxidation state. It is difficult to imagine that the M^{1+} states are present in excess for poly(CuTTO) and poly(NiTTO).
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Synthesis and Characterization of Bifunctional Ion-Exchange/Coordination Resins

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ABSTRACT: The synthesis of bifunctional resins that complex metal ions via the mechanisms of ion exchange and coordination is detailed. These resins form the second class of polymer-supported complexing agents for specific metal ion extractions within the recently detailed dual mechanism bifunctional polymer category. This series of resins incorporates phosphonic acid groups as the ion-exchange ligand and a varying coordination ligand that allows the different resins to be selective for different metal ions. The development of resins with phosphonic acid/phosphonate ester ligands and phosphonic acid/tertiary amine ligands on a polystyrene support is described.

Introduction

The selective complexation of a targeted metal ion by a given ligand is an important objective for many applications, including catalytic,[1] chromatographic,[2] and metal ion recovery[3] processes. The ion-exchange reaction is an extremely versatile reaction and one that is well-suited to the complexation of cations and anions through electrostatic binding. The strongly acidic sulfonic acid cation-exchange resin has played a central role in metal recovery processes due to its exchange strength in acidic solutions.[4] The classic works of Boyd and his co-workers,[5] though, have shown that the ion-exchange reaction alone does not have a wide enough range in the free energy of reaction to allow for selectivity: for example, the change in enthalpy of reaction for the sulfonic resins with alkali metal ions is only 1.5 kcal/mol. The inability of the sulfonic resin to differentiate among many ions for a given ion can thus obviate its use for practical recovery processes[6] requiring the selective absorption of valuable or toxic metal ions in a background of innocuous ions present at much higher concentrations. Additionally, a small value for the free energy of reaction implies that the metal ion can be lost to the environment in catalytic applications since the binding would be relatively weak. Ion-exchange resins are very important to metal ion complexation reactions due to their hydrophilicity, accessibility, and high capacity, but the synthesis of a polymer with a greater degree of selectivity would prove important to different applications.

Ions are capable of undergoing many reactions in addition to simple ion exchange such as reduction, coordination/chelation, and precipitation.[7] These reactions can be quite specific for certain metal ions depending on the coreactant: for example, with a series of reducing agents, a metal ion can be unaffected, be reduced to a lower ionic valence state, or be removed from solution in its metallic form; with a series of anions, a metal ion can remain free (i.e., solvated), complexed to various degrees, or precipitate from solution. It therefore follows that the introduction

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