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Electrical conductive and magnetic properties of conjugated tetrathiolate nickel polymers

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SUMMARY

Three tetrathiolate (tetrathiafulvalenetetrathiolate, ethylenetetrathiolate, and butadienetetrathiolate) nickel polymers are prepared. The polymers contain mixed valence Ni ions and are ESR active based on low-spin d^8 Ni(III) species. Magnetic susceptibility measurement in the range of 30 - 60 K suggests an antiferromagnetic interaction between the Ni ions in the polymers. Below 30K a weak ferromagnetic interaction is observed. Chemically oxidized polymers are ESR inactive, while electrical conductivity is greatly enhanced.

INTRODUCTION

Dithiolate metal complexes have received much research attention[1-3], because strong $d\pi$ -$p\pi$ interaction between central metal ion and conjugated ligands and a number of stable oxidation states is observed for these complexes. Coordination polymers of transition metal ions and tetrathiolates have also been investigated: metallopolymers containing π-conjugated tetrathiolate as bridging ligands such as benzenetetrathiolate[4], naphthalenetetrathiolate[5], tetrathiafulvalenetetrathiolate[6,7], ethylenetetrathiolate[8], butadienetetrathiolate[9]. It has been reported that these polymeric tetrathiolate metal complexes show high conductivity after their partial oxidation and show electrical and magnetic interactions between metal ions through conjugated tetrathiolate ligands[6]. Cassoux et al. have reported that tetratiafulvalenetetrathiolate nickel polymer shows high conductivity (σ_{300K} = 20 S cm^{-1}) upon bromine oxidation as well as unusual ferromagnetism at ordinary temperature[6].

In this paper, we carefully reprepared tetratiafulvalenetetrathiolate nickel(TTFTT-Ni), ethylenetetrathiolate nickel (ETT-Ni), and butadienetetrathiolate nickel(BTT-Ni) polymers. Magnetic property of these polymers was studied by ESR and magnetic susceptibility measurement in comparison with a low molecular bis(isotrithionedithiolate) nickel ($(DMIT)_2$-Ni) complex. These polymers were chemically oxidized with various oxidizing reagents, and electrical conductivity of the the resultant oxidized polymers were also discussed in connection with degree of partial oxidation.

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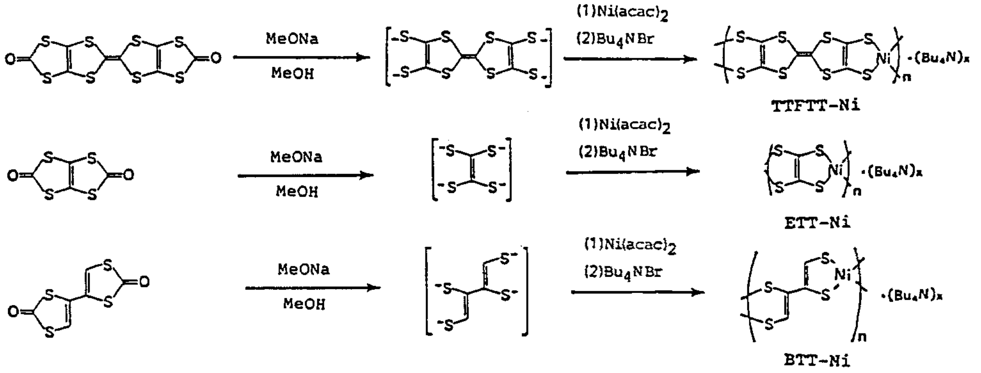

Scheme 1

EXPERIMENTAL

Materials

Bis(carbonyldithio)tetrathiafluvalene, 1,3,5,6-tetrathiapentalene-2,5-dione, 4,4'-bis(1,3-dithiole-2-one) were prepared as in the lit(7,10,9), respectively. All reactions were carried out under nitrogen atmosphere or under reduced pressure. Solvents were freshly distilled and degassed prior to use.

Tetrathiafulvalenetetrathiolate nickel (TTFTT-Ni) polymer was prepared as follows. Bis(carbonyldithio)tetrathiafluvalene is reacted with 4 mol equiv. of sodium methoxide in methanol for 10 hr at room temperature (Scheme 1). To the resulting solution, 1 mol equiv. of anhydrous bis(acetylacetonate)nickel was added, and the solution was stirred for 1 hr. After the addition of a methanolic solution of 2 mol equiv. tetra-*n*-butylammonium bromide, the black powder precipitated was collected, washed with water, methanol, acetone, and ether, and dried in vacuo. Ethylenetetrathiolate nickel (ETT-Ni) and butadienetetrathiolate nickel (BTT-Ni) polymers were prepared from 1,3,5,6-tetrathiapentalene-2,5-dione, and 4,4'-bis(1,3-dithiole-2-one) in a similar manner as the TTFTT-Ni polymer. Bis(iso-tri-thionedithiolate) nickel ($(DMIT)_2$-Ni) complex was prepared as in the lit(11).

Elemental analysis was carried out to estimate the composition of the polymers.

Chemical oxidation of the polymers

An acetone solution of tetracyanoethylene (TCNE) or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) as an oxidizing agent was added to a suspension of the polymer, and the mixture was stirred for 2 hr at room temperature. In the case of bromine or iodine oxidation, a methanol solution was used and the mixture was stirred at 0°C for 2hr. Oxygen oxidation was carried out by bubbling oxygen gas for 10 min. Black powder precipitated was collected and washed with water, methanol, acetone and ether, and dried in vacuo.

Measurements

IR and ESR spectra were measured with JASCO-IR-810, and JEOL JES-FE2XG, respectively. Magnetic susceptibility was measured with a Faraday-type magnetic lever using Gd_2O_3 as a standard. The diamagnetic corrections for the TTFTT-Ni and ETT-Ni polymers were estimated to be -4.1×10^{-4}, -2.4×10^{-4} emu/mol, respectively, using Pascal's constants. Temperature independent paramagnetism 2.5×10^{-4} emu/mol was used for the calculation. Electrical conductivity was measured on a pressed disk with two-probe technique for low conductive samples and with four-probe technique for high conductive ones, respectively.

Table 1 Elemental analysis of the tetrathiolate Ni polymers

Polymer	Element	Chemical species			
		Obtained (Found)	Dianion (Calcd.)	Monoanion (Calcd.)	Neutral (Calcd.)
TTFTT-Ni	C(%)	44.63	52.33	41.95	18.61
	H(%)	6.42	8.32	5.76	0
	N(%)	2.48	3.21	2.22	0
	Ni(%)	9.0 ($X^a \approx 1.20$)	6.73	0	15.15
ETT-Ni	C(%)	42.70	58.68	47.68	11.39
	H(%)	6.52	10.43	8.00	0
	N(%)	2.64	4.03	4.09	0
	Ni(%)	14.7 ($X \approx 0.73$)	8.44	12.95	27.83
BTT-Ni	C(%)	40.19	59.89	50.10	20.27
	H(%)	5.13	10.33	7.99	0.85
	N(%)	1.68	3.88	2.92	0
	Ni(%)	13.9 ($X \approx 0.40$)	8.13	12.24	24.76
$(DMIT)_2$-Ni	C(%)	48.80	48.74	38.08	15.96
	H(%)	7.69	7.75	5.23	0
	N(%)	2.98	2.99	2.02	0
	Ni(%)	6.4 ($X \approx 2.00$)	6.27	8.46	13.00

[a] X indicates molar ratio $[Bu_4N]/[\text{tetrathiolate unit}]$

RESULTS AND DISCUSSION

The prepared polymers contained tetra-*n*-butylammonium ion, whose amount corresponds to the average oxidation number of the Ni ion: e.g. molar ratios of $[Bu_4N]$ [tetrathiolate unit](abbreviated as X) =2 and 1 indicate a dianion tetrathiolate nickel complex or a Ni(II) species and a monoanion tetrathiolate nickel complex or a Ni(III) species, respectively, and X=0 means the supposedly neutral complex(Table 1). The polymers were auto-oxidized during the complex or polymer formation even under anaerobic condition, while the corresponding complexation with DMIT gave an unoxidized $(DMIT)_2$-Ni complex. A partial redox reaction of Ni with tetrathiolate take place during the polymer formation.

Dithiolate metal complexes show three characteristic IR absorptions in addition to ones being attributed to the substituents of ligands and the cations in charged species. It has been reported that one of them assigned to the perturbed C=C stretching mode varies with the overall charge on the complex and that a C=C stretching frequency number of the $(DMIT)_2$-Ni complexes decreases with the increasing degree of oxidation[13]. The TTFTT-Ni polymer showed the broad absorption at 1270 cm^{-1} for the polymer with X=1.20 which shifted to 1220 cm^{-1} for the chemically oxidized polymer with X=0.15, while the ETT- and BTT-Ni polymers showed a few IR bands in this region and definitive assignment of these bands was difficult. This IR shift of the TTFTT-Ni polymer suggests that the polymer is oxidized in a similar process of $(DMIT)_2$-Ni, i.e. the oxidation is caused by the removal of electron from either the metal ion or the conjugated thiolate ligand.

The $(DMIT)_2$-Ni complex is ESR silent because of low-spin d^8 electron configuration of the Ni ion. The chemically oxidized $(DMIT)_2$-Ni complex (X=0.98) becomes ESR active, based on low spin d^7 configuration of the Ni ion. $(DMIT)_2$-Ni(X=0.05) showed very weak absorption in ESR spectrum due to residual Ni(III) species. Polymers are ESR active without chemical oxidation, indicating the formation of Ni(III) species. Intensities of the ESR signal for the polymers decreased as oxidation proceeded near to X=0.

Magnetic susceptibility measurement was carried out for the ESR active TTFTT-Ni(X=1.20) and ETT-Ni(X=0.73) complex in the temperature range of 60 and 4 K. Magnetic data are summarized in Table 2. The $1/\chi$ vs. T plots show linear relationships obeying a Curie-Weiss law in the range of 60 and 30 K. The θ values were estimated by extrapolating these linear relationships. The extrapolated θ values given in Table 2 suggest an antiferromagnetic interactions between the Ni ions through the bridging conjugated thiolate ligand in these polymers. Below 30K slight deviation from Curie-Weiss law was observed. Indeed the $_{eff}$ values become larger at 4.2K than at 60.0K. These data suggest a weak ferromagnetic interaction at lower temperature. For the ETT-Na(X=0.31) complex Cassoux et al. reported similar weak ferromagnetic the Ni ions through an interchain coupling[8]. However, the ferromagnetic behavior at ordinary temperature reported for the TTFTT-Ni polymer[6] could not be observed for the polymer prepared in this paper.

Table 2 Magnetic susceptibilities and magnetic moments of the tetrathiolate Ni polymers

Polymer	X	X x 10^2(emu/mol)		μ_{eff}(B.M.)		Weiss constant
		4.2(K)	60.0(K)	4.2(K)	60.0(K)	θ(K)
TTFTT-Ni	1.20	2.75	0.488	2.12	1.68	-16
ETT-Ni	0.73	3.65	0.441	1.80	1.51	-7

*Extrapolated from the $1/\chi$ vs. T plot in the range of 60 and 30K.

Electrical conductivity of these polymers was listed in Table 3. The conductivity increases with the oxidation of the polymers except of the BTT-Ni polymers, and the oxidized TTFTT-Ni polymers shows the highest conductivity. The TTFTT-Ni polymer oxidized with bromine gives 20 S cm^{-1}, which is comparable with that previously reported[6]. This result suggests that the conjugated coplanar TTFTT moiety plays an important role for the electrical property of the complex. The unoxidized BTT-Ni polymer is low conductive, while X is lower than those of the TTFTT- and ETT-Ni polymers probably due to the located conjugated system in the ligand. Elemental analysis data of the oxidized BTT-Ni polymers were not stoichiometric, suggesting some decomposition of the polymer through the oxidation process.

Table 3 Electrical conductivity of the partially oxidized tetrathiolate Ni polymers

Polymer	Oxidizing reagent	X	σ (S/cm)	Ref.
TTFTT-Ni	none	1.20	$3x10^{-4}$	
	TCNE	0.24	3x10	
	DDQ	0.25	4x10	
	O_2	0.29	6x10	
	Br_2	0.15	2x10	
	I_2	0.12	5x10	
	Br_2	—	20	6)
	—	—	30	7)
ETT-Ni	none	0.73	$6x10^{-5}$	
	TCNE	0.22	2	
	DDQ	0.25	1	
	O_2	0.30	2	
	Br_2	0.23	2	
	I_2	0.27	$7x10^{-1}$	
	I_2	0.16	0.9	8)
BTT-Ni	none	0.40	$3x10^{-8}$	
	DDQ	—*	$5x10^{-8}$	
	I_2	—*	$1x10^{-7}$	
$(DMIT)_2$-Ni	none	2.00	$5x10^{-10}$	
	TCNE	0.05	$3x10^{-3}$	
	DDQ	0.02	$6x10^{-4}$	
	O_2	0.95	$3x10^{-8}$	
	Br_2	0.05	$6x10^{-4}$	
	I_2	0.06	$5x10^{-4}$	
	Br_2	—	1	12)

*Stoichiometric analysis was not obtained.

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