

Electrically Conducting Transition Metal Complexes of Tetrathio-oxalate

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Oligomeric complexes of tetrathio-oxalate with Ni^{II}, Cu^{II}, and Pd^{II} have been synthesized to yield materials having high electrical conductivities of up to 20 S cm⁻¹.

One of the main disadvantages of organic conjugated polymers which become conducting upon redox doping is their instability in air. This is generally attributed to the extreme doping potentials necessary for the creation of charge carriers. Polymers composed of transition metal ions complexed with conjugated ligands can possess unfilled molecular orbitals and be intrinsic conductors, eliminating the need for these doping processes.

Conducting metal complexes with tetrathionaphthalene,¹ tetrathiafulvalene tetrathiolate,² and ethylene tetrathiolate³ have been reported, but the reaction of these tetrafunctional ligands with bivalent metal ions necessarily results in network products which are difficult to purify.† The difunctional tetrathiosquarate ligand forms linear chains with Ni^{II}, Pd^{II}, and Pt^{II},⁴ but the products have disappointing low room temperature conductivities of 5 × 10⁻⁴, 3 × 10⁻⁷, and 6 × 10⁻⁷ S cm⁻¹, respectively.

We report here the synthesis and characterization of highly conducting linear complexes from the difunctional tetraethylammonium salt of tetrathio-oxalate (TEATTO), [Et₄N]₂⁺[C₂S₄]²⁻, with Ni^{II}, Cu^{II}, and Pd^{II}.

TEATTO was prepared in ca. 50% yield by the electrochemical reduction of CS₂ in MeCN at 5 °C saturated with Et₄NBr.⁵ The reaction was carried out at a mercury electrode of ca. 50 cm² at -1.0 V vs. Ag/AgI. Recrystallization from methanol yields red-orange platelets [m.p. 187–188 °C, lit. 186–189 °C; i.r. (KBr) 3000(m), 2970(s), 2940(m), 1452(s), 1400(s), 1350(m), 1305(m), 1180(s), 1030(m), 983(s), 798(s), 760(s), and 740(s) cm⁻¹; u.v.–visible λ_{max}. (MeOH) 278 and 342 nm].‡ TEATTO is unstable in air and thus all reactions and handling were carried out under an inert atmosphere.

Polymerization reactions of TEATTO with M^{II} were carried out using 1:1 stoichiometry of reactants as shown using Ni(NO₃)₂ in Figure 1. The polymer chain is represented as a metallopentacycle, instead of a metallotetracycle, by comparison with previously synthesized bimetallic tetrathio-oxalate complexes.⁶

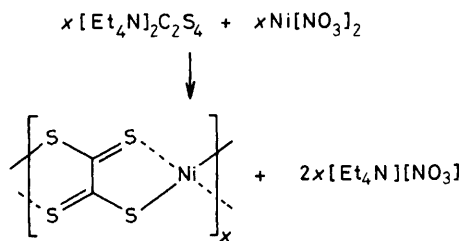


Figure 1. Reaction scheme for synthesis of [NiC₂S₄]_x.

† We have prepared (NiC₂S₄Na₂)_x with a σ value of 0.1 S cm⁻¹ but it is an intractable solid.

‡ Satisfactory elemental analysis was obtained.

Reaction of TEATTO at 25 °C with Ni(OAc)₂ · 4H₂O in methanol yields an insoluble black powder. Elemental analysis was consistent with the structure [(C₂S₄Ni)₃C₂S₄]²⁻[Et₄N]₂⁺. The product is actually an oligomer having a fortuitous integer average degree of polymerization, \overline{DP} , of 3.0. Efforts to increase the \overline{DP} through careful stoichiometric control were ineffective. The chain length is controlled by the low solubility of the rigid chains which precipitate out during reaction.

Oligomers of [NiC₂S₄]_x have conductivities (σ) of 5 to 20 S cm⁻¹ and low thermoelectric power coefficients (TEP) of -20 μV K⁻¹. Conductivity was measured using the four-probe technique on pressed pellets and the TEP was measured by monitoring the voltage across a sample, pressed between copper blocks, having a 2–5 °C temperature difference. The TEP shows the majority carriers to be negatively charged. The conduction is electronic as determined by charge polarization experiments. Absorption or reflection by the carriers gives no transmission of i.r. radiation, even in dilute KBr dispersions. The complex does not melt and is amorphous to X-ray diffraction. It is only slightly soluble in polar aprotic solvents, probably because of a fractionation effect. Conductivity is thermally activated with an activation parameter E_a, of 0.020 eV between -196 and +25 °C. Interfacial polymerization techniques did not produce polymers with a higher \overline{DP} or σ at room temperature.

The reaction of Cu(NO₃)₂ · 3H₂O with TEATTO in an 80:20 mixture of N,N-dimethylformamide (DMF)–methanol at 80 °C yields a black insoluble powder. Comparison of the copper to nitrogen content suggests an oligomer with a \overline{DP} of 7–8 but the overall analysis is complicated by the presence of both Et₄N⁺ and NO₃⁻ end groups.

Oligomer [CuC₂S₄]_x has a σ value of 1 S cm⁻¹, a low TEP of -10 μV K⁻¹, and is also highly i.r. absorbing. A plot of log σ vs. T⁻¹, Figure 2, shows the material to behave as a semiconductor with an E_a of 0.030 eV at low temperature which changes to 0.050 eV between -40 and +25 °C. The same data is linear when plotted against T^{-1/2} but owing to the heterogeneous nature of the pressed pellets and the presence of interparticle contact resistance we hesitate to propose a specific conduction mechanism.

Iodine oxidation of both [NiC₂S₄]_x and [CuC₂S₄]_x causes a 10³ and 10¹ fold reduction in σ, respectively, indicative of a compensation effect of the negative carriers by the oxidant. The effect is partially reversible as evacuation restored the σ value to about half its original value in both materials.

The reaction of PdCl₂ with TEATTO in an 80:20 mixture of DMF–methanol at 80 °C yields a black insoluble powder with a σ value of 1 S cm⁻¹ and TEP of -50 μV K⁻¹. It is amorphous and highly i.r. absorbing. It has a similar oligomeric structure as the Ni and Cu complexes having a \overline{DP} of 4.5, with tetrathio-oxalate end groups. Full elemental analysis gave results consistent with the formulation C₈H₂₀N-[(C₂S₄Pd)_{4.5}C₂S₄]_xC₈H₂₀N.

These [MC₂S₄]_x materials are air stable. After 60 days exposure there was no measurable change in the σ value of the

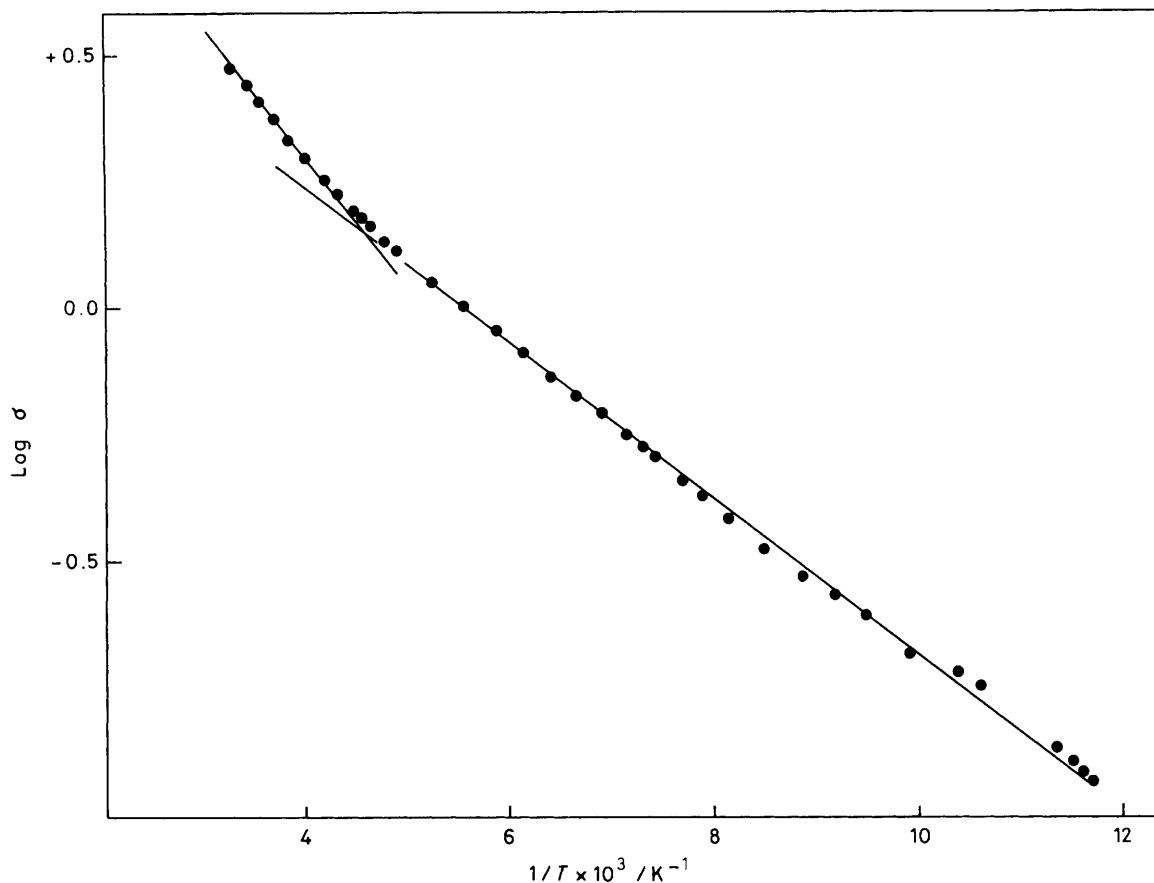


Figure 2. Arrhenius plot for the conductivity of $[\text{CuC}_2\text{S}_4]_x$.

Pd complex while the σ value of the Cu and Ni complexes decreased only slightly.

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