A New Organic Conducting Material Derived from 1,4-Diaminoanthraquinone

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Introduction

Conducting organic materials have drawn considerable attention due to the exciting possibilities of creating metallike conductivity and superconductivity and the potential applications of their interesting electrical, optical, and magnetic properties. The discovery of metallic conductivity in molecular organic systems was a breakthrough that aroused the interest of chemists, physicists, and theorists.[1] High conductivities have also been achieved in oxidized/reduced polymers such as phthalocyanines,[2] polyacetylenes,[3] poly(*p*-phenylenes),[4] polypyrrole,[5] and polyaniline.[6-8] Several planar coordination oligomers possessing intrinsic electrical conductivity have been reported in the literature.[9] Coordination complexes of 1,4-diaminoanthraquinone with different metal atoms have been studied recently.[10] Here, we report the synthesis, characterization, and low-temperature conducting properties of a novel conducting material formed by oxidizing 1,4-diaminoanthraquinone (1,4-DAAQ) with cerium(IV). The complex formed is stable at ambient conditions with very interesting conducting properties.

Results and Discussion

1,4-DAAQ oxidized with different metal atoms gives rise to conducting coordination polymers consisting of difunctional ligand molecules linked by metal atoms. They are generally insoluble and precipitate from the reaction media as oligomers with degrees of polymerization less than 20 due to interaction between chains with a metal content as high as 22.2% (monomer/$M^{2+} \approx 1$). On the other hand, elemental analysis of the complex formed by oxidizing 1,4-DAAQ with ceric(IV) ammonium nitrate does not indicate the presence of cerium (Table I).

In the IR spectrum of the complex (Figure 1), a large broad adsorption peak is observed from 4000 to 1700 cm^{-1}. An absorption of this type is frequently encountered in electrically conducting organic materials and is due to electronic transitions from the valence band to the conduction band.[11] The only other significant peaks occur at 1635 and 1355 cm^{-1}. The former peak is the quinone carbonyl stretching frequency shifted from 1610 cm^{-1}, and the one at 1355 cm^{-1} corresponds to the nitrate group. ESR of the sample was recorded at 300 and 77 K. At 77 K (Figure 2) a broad signal is observed, centered at g = 1.982 with an indication of some hyperfine interaction. However, at higher temperatures a very broad band is observed with a reduced intensity probably due to increased electron exchange and delocalization.

The conducting complex obtained is highly insoluble in common solvents except in DMSO, making spectroscopic characterization difficult. The NMR spectrum obtained in DMSO-d_6 of a freshly dissolved sample gives rise to signals corresponding to that of the starting material except for the broadening presumably due to electron exchange

Table I
Conductivity, Elemental Assay, and Empirical Formula for the Complex

C %	H %	N %	Ce %	formula	σ_{rt}, S/cm
59.6	3.91	12.37	≤0.001	$C_{14}H_{11}N_{2.47}O_{4.3}$[a]	0.186

[a] Calculated by difference.

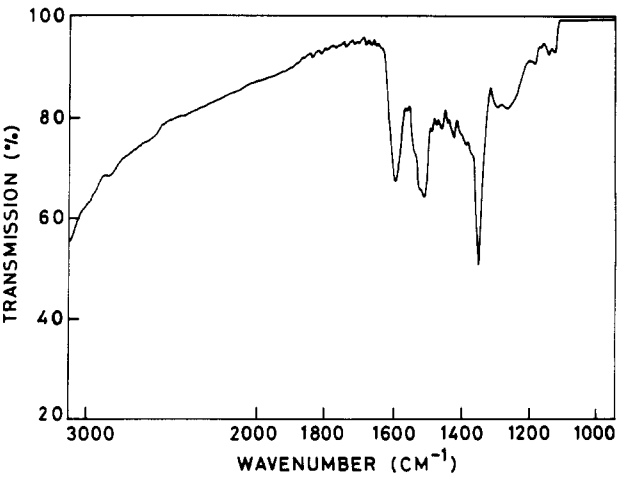

Figure 1. IR spectrum of the Ce^{4+}-oxidized 1,4-DAAQ complex.

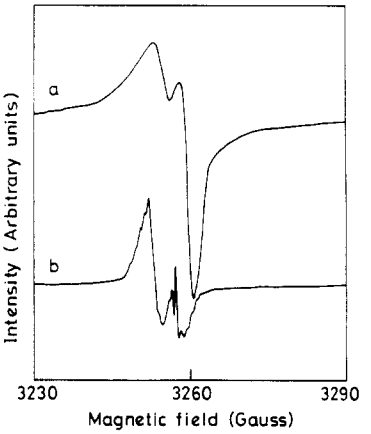

Figure 2. ESR spectrum of the Ce^{4+}-oxidized 1,4-DAAQ complex: (a) at 300 K, receiver gain was 5×10^3; (b) at 77 K, receiver gain was 2.5×10^3.

in solution. The solid-state ^1H NMR (Figure 3) also revealed broadening and upfield shifting of the lines centered at +5.65 and −0.416 ppm in the starting material. X-ray diffraction of the complex shows it to be crystalline (Figure 4). The most intense peak corresponds to a d-spacing of 10.4 Å, whereas in the starting material the d-spacing is 13 Å. The crystallite size estimated from the peak broadness by using the Scherrer formula[12] ranges from 200 to 275 Å.

From the above data it appears that the insoluble oligomer formed by oxidation with cerium(IV) carries a charge

$$[1,4\text{-DAAQ}]_n^{(1.5)n+}[NO_3]_{0.5n}^{-}[OH]_n^{-}$$

with NO_3^- and OH^- as counterions. These chains form acceptor and donor stacks due to interaction between the oxidized and unoxidized portions of the chain giving rise to high conductivity.

The temperature dependence of dc electrical conductivity of the complex is shown in Figure 5. The plot of ln ρ versus $1/T$ takes a curve form instead of a linear form over the given temperature range. For semiconducting

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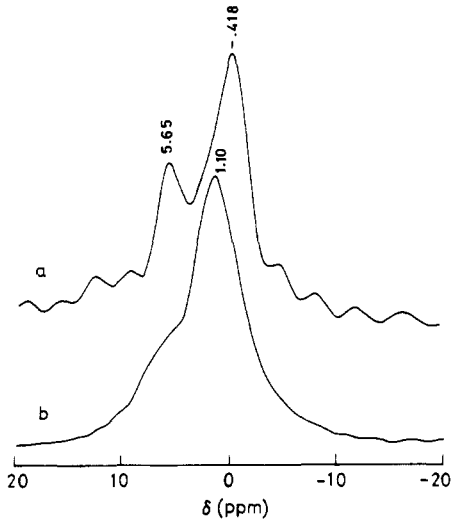

Figure 3. ^{1}H solid-state NMR: (a) starting material; (b) conducting complex formed through oxidation of 1,4-DAAQ with Ce^{4+}.

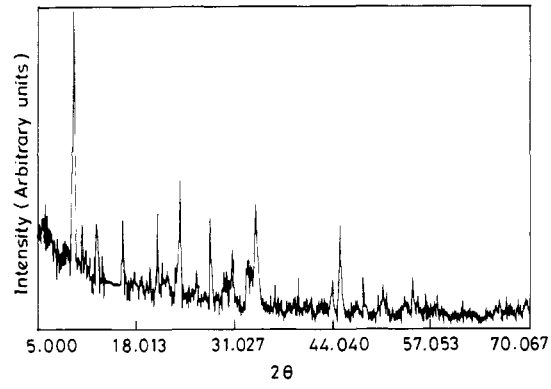

Figure 4. Powder X-ray diffraction of the Ce^{4+}-oxidized 1,4-DAAQ complex.

materials these plots should yield straight lines over the given temperature range, obeying the equation $\rho = \rho_0 \exp(E/2kT)$, where ρ is the resistivity at absolute temperature T, ρ_0 is a constant, E is the energy gap, and k is Boltzmann's constant, but the present conductivity data do not fit the above equation.

Variable-range hopping model was suggested by Mott[13] to be the dominant transport mechanism for conductivity in disordered materials at low temperatures. Mott's formula for the hopping conductivity σ at Fermi level E_F is given by

$$\ln \sigma = \text{constant} \times \left[\frac{\alpha^n}{kN_n(E_F)\,T}\right]^{(1/1+n)}$$

where $N_n(E_F)$ is the density of states at the Fermi level for 2- or 3-dimensional hopping ($n = 2$ or 3, respectively), k is Boltzmann's constant, and α is the inverse electron localization length.

From experimental observations, in both doped crystalline semiconductors and amorphous materials, the conductivity can be fitted to the following expression:

$$\sigma = A \exp(-B/T^m)$$

Efros and Shklovskii[14] showed that when Coulombic interaction between electrons is taken into account, the value predicted for m is $^1/_2$. However, Theye et al.[15] found that in evaporated and sputtered amorphous germanium they could not distinguish between $m = {}^1/_2$ and $m = {}^1/_4$. Figure 6 shows that the present conductivity variation

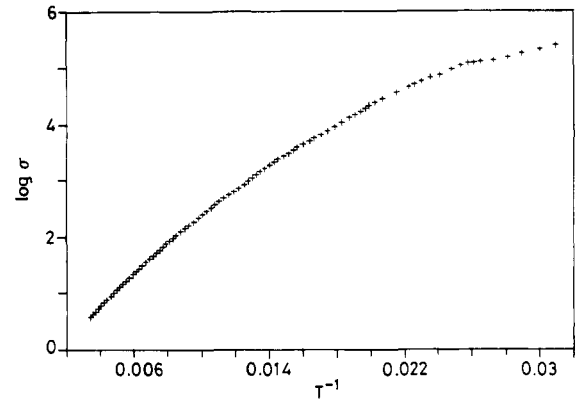

Figure 5. Variation of resistivity as a function of temperature: $\ln \rho$ vs T^{-1}.

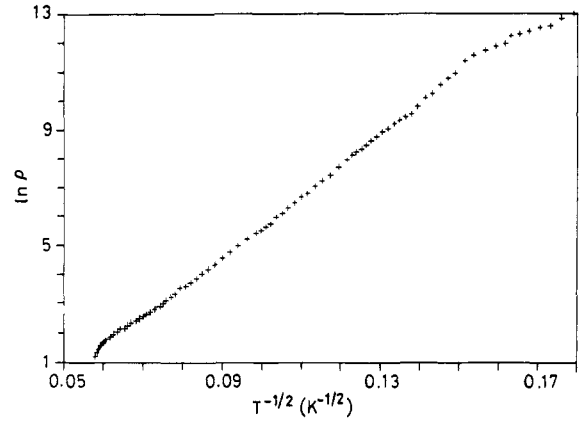

Figure 6. Variation of resistivity as a function of temperature: $\ln \rho$ vs $T^{-1/2}$.

fits the relation $\ln \rho = \text{constant} \times T^{-1/2}$ better. Thus the deviation from $T^{-1/3}$ predicted by Mott is attributed to the Coulombic interaction between electrons which causes a depletion of the single-particle DOS near the Fermi energy.

This is the first report of a highly conducting complex obtained from 1,4-DAAQ without incorporating a metal. Thus cerium is unique in that it oxidizes 1,4-DAAQ without coordinating with the product.

Experimental Section

1,4-Diaminoanthraquinone is recrystallized several times in acetone. All other chemicals used are of reagent grade and used without further purification. 1,4-Diaminoanthraquinone (4.2 mmol) is dissolved in 25–30 mL of dimethylformamide. To this solution is added ceric ammonium nitrate (4.2 mmol). The mixture is allowed to stand for 1 h. The precipitate formed is collected and washed several times with water and acetone and finally with methylene chloride. The reddish-brown powder is dried at 50 °C in a vacuum oven for 16 h (yield 58%). The complex obtained exhibits a high conductivity comparable with that of the coordination complex formed by oxidizing 1,4-DAAQ with copper.[10] C,H,N analysis is obtained from CarloErba Strumentisation elemental analysis Model 1106. The absence of cerium is confirmed through several spot tests and inductive coupled atomic emission spectroscopy (ICP–AES) Plasmascan Model 8410 for which the detection limit is 2 ppm.

The conductivity of the pellets made by compressing the powder at a pressure of 4 kbar is measured using a standard four-probe technique (Vanderpauw). Contacts are made with silver paste. The variation of the conductivity with temperature is studied using a commercial Janis liquid-helium cryostat.

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Registry No. 1,4-DAAQ (homopolymer), 105469-86-1; ceric ammonium nitrate, 598-30-1.