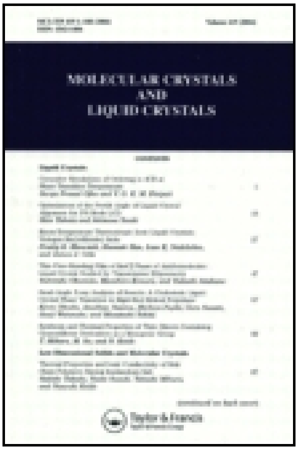

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Physical Properties, Electrical Conductivity and Crystal Structure of the Dadmtani-TCNQ Complex

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PHYSICAL PROPERTIES, ELECTRICAL CONDUCTIVITY AND CRYSTAL STRUCTURE OF THE DADMTANi-TCNQ COMPLEX

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Abstract The crystal and molecular structure, electrical conductivity, infrared spectra and magnetic susceptibility of the complex 6,13-diacetyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenenickel (II)-7,7,8,8-tetracyano-p-quinodimethane (DADMTANi-TCNQ) have been measured. DADMTANi-TCNQ crystallizes in the monoclinic space group $P2_1/n$ with a=7.111(7), b=14.191(3), c=13.062(4), β=93.21(2)°; z=2. The molecules are arranged in alternated stacks. The electrical conductivity of the complex measured along the shortest axis of the crystal is 10^{-4} ohm^{-1} cm^{-1}. This low value, the magnetic susceptibility and IR data are related to the crystal structure.

INTRODUCTION

Change transfer complexes of 7,7,8,8-tetracyanoquino-p-dimethane (TCNQ) with a variety of electron donors have been extensively studied[1]. Their properties range from metallic to insulating depending on both, the degree of charge transfer between the molecules and the way they are stacked.

We have been studied the inorganic complex, 6,13-diacetyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenenickel (II) (DADMTANi) and have found that its electrical conductivity increases upon doping with iodine[2]. This effect is probably due to stacking of the molecules. Because of the planarity of the system, the presence of delocalized π electrons and a metal atom, DADMTANi appears as an interesting compound for the formation of charge-transfer complexes with TCNQ.

We report here the complex DADMTANi-TCNQ, its physical properties and their correlation to its crystal and molecular structure.

EXPERIMENTAL

DADMTANi was synthesized and purified according to the literature[3]. Comercial TCNQ was recrystallized from chloroform.

DADMTANi and TCNQ (1:1) were heated for 15 minutes in chloroform. Slow cooling gave black crystals suitable for x-ray diffraction studies and conductivity measurements.

Infrared spectra of KBr pellets of DADMTANi-TCNQ were performed on a Nicolet MX-5 Fast Fourier Transform Spectrophotometer in the 4600-400 cm^{-1} region.

Magnetic susceptibility measurements were performed on a Cahn Faraday balance at room temperature.

Electrical conductivity measurements were carried out on single crystals with contacts made of electrodag. The electric field was applied along the stacking axis *a*. The conductivity was studied as function of temperature in the 25-80°C range.

Crystal data are as follows: black prismatic crystal 0.15 x 0.23 x 0.44 mm., monoclinic, $P2_1/n$, a=7.111(1), b=14.191(3), c=13.062(4) Å, β=93.21(2)°, V=1316.0(5) $Å^3$, D_x=1.43 Mg m^{-3}, Z=2, T=293 K.

Complete three dimensional data were collected to the limit of $2\theta=45°$ for MoK_α using a Nicolet R3 four-circle diffractometer. 1886 reflections were measured out of which

1405 had intensities greater than 2.5σ. The structure was solved by heavy-atom method and refined by a cascade matrix least-squares techniques to R=0.045. All computations were performed on a Nova 4 computer and plots drawn on a Tektronix plotter with the SHELXTL system of programs[4]

RESULTS AND DISCUSSION

Electrical conductivity of crystals of DADMTANi-TCNQ was measured by the two probe technique. The conductivity varies with temperature exhibiting ohmic behaviour. The values range from 10^{-4} ohm^{-1} cm^{-1} at room temperature to 5×10^{-2} ohm^{-1} cm^{-1} at 80°C. The activation energy Ea was determined using the expression $\sigma=\sigma_0 \exp(-E_a/kT)$ and its value is 0.37eV. These values are typical of a semiconductor and are similar to those reported for TCNQ complex salts[5].

Magnetic susceptibility measurements on the complex do not show net spin susceptibility indicating no charge-transfer. Infrared spectra does not present the characteristic charge-transfer band typical for TCNQ complex salts. Most of the weak absorptions appear at the same frequency as in the IR spectra of the isolated molecules. It shows bands typical for neutral TCNQ[6]. The most prominent bands are located at the C-H streching vibration region at about 3000 cm^{-1}.

It is possible to obtain the degree of ionicity from the dependence of the vibrational frequency versus the charge density. The mode $\nu_2 a_g$ of TCNQ suffers a shift in ionized CT complexes. In neutral TCNQ this mode is found at 2229 cm^{-1}, and in Rb-TCNQ it is observed at 2187 cm^{-1}. In the DADMTANi-TCNQ complex this mode is observed at about

2221 cm^{-1}, suggesting that there is no net charge-transfer in this case.

The crystal and molecular structure determination of DADMTANi-TCNQ provides a satisfactory interpretation of the properties of this complex. Figures 1 and 2 show a general view of the molecular packing. The structure consists of stacks in which DADMTANi and TCNQ molecules alternate in infinite columns parallel to axis *a* (Figure 3).

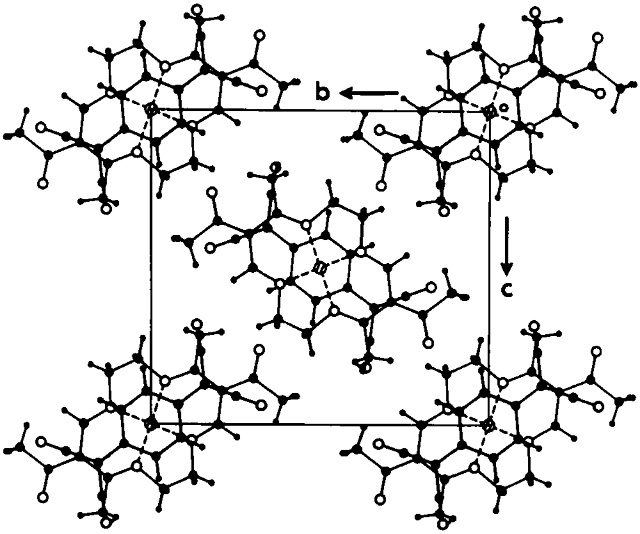

FIGURE 1. Projection of the structure of DADMTANi-TNCQ along *a* axis.

The dihedral angle between the DADMTANi and TCNQ mean planes is 6.1(5)°. The interplanar distance is 3.45(5) Å indicating that the interactions between the molecules may be due to van der Waals forces.

Bond lengths and angles for non-H-atoms of the two molecules are indicated in figure 4.

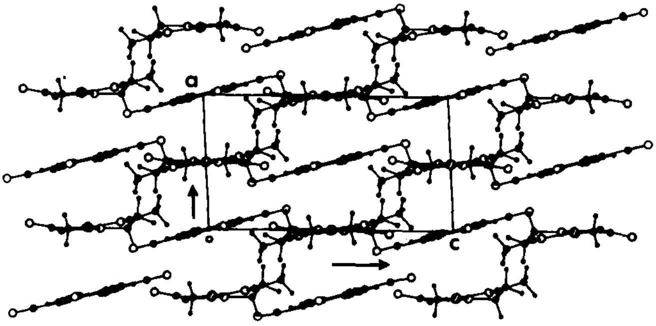

FIGURE 2. Projection of the structure of DADMTANi-TCNQ along *b* axis.

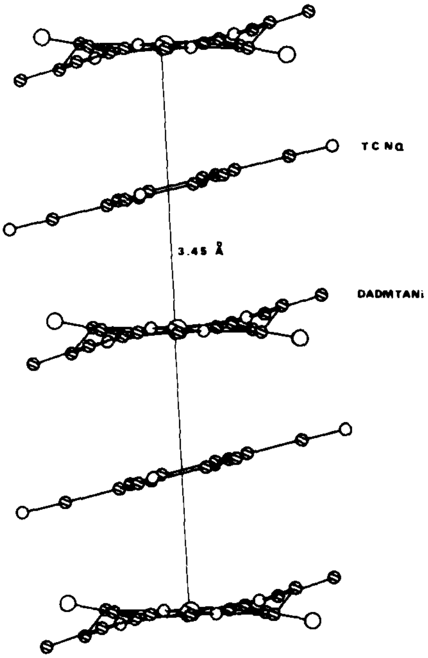

FIGURE 3. Projection down the *b* axis of the stacking of the DADMTANi and TCNQ species along the *a* axis.

By comparison of the quinonoid bond lengths in DADMTANi -TCNQ (1.372(6) Å), in neutral TCNQ (1.374 Å)[7] and in TCNQ

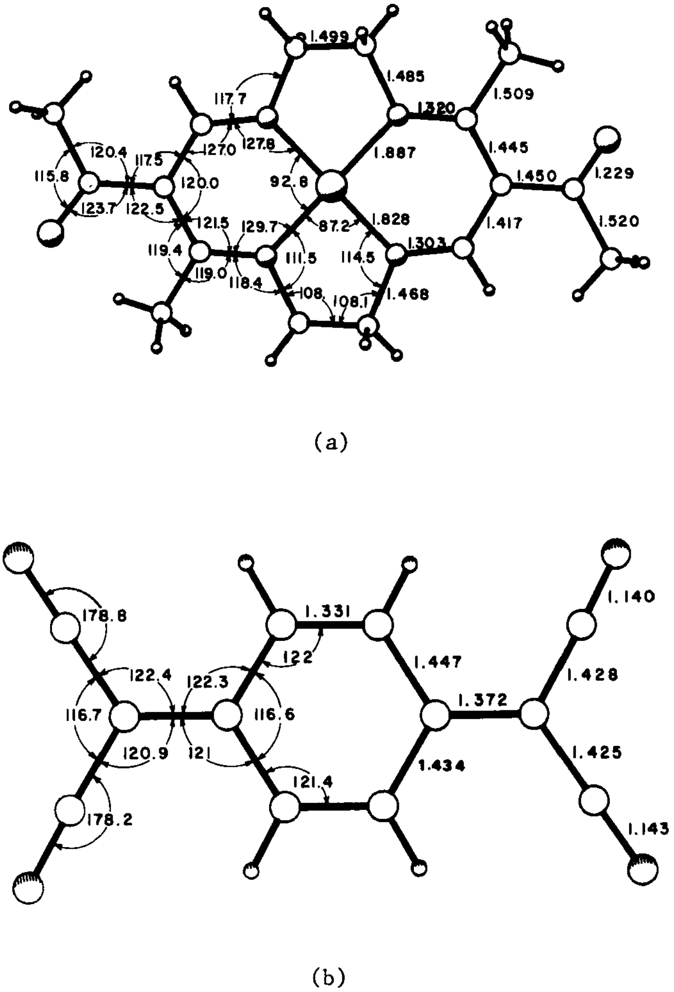

FIGURE 4. Bond lengths (Å) and bond angles (°) for DADMTANi (a) and TCNQ (b).

charge-transfer complexes (*e.g.* in TTF-TCNQ, 1.402 Å)[8] we can consider that the TCNQ species of this system is neutral.

We conclude then, that the poor conductivity of the DADMTANi-TCNQ complex, the data obtained from the IR spectra and the lack of magnetic susceptibility all are related to the alternate stacking structure of the complex. The absence of charge-transfer is confirmed by the short length of the quinonoid bond in TCNQ.

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