A Novel Conductive Molecular Solid Composed of Tetraaza Nickel Complexes

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The studies of quasi-one-dimensional conductive materials composed of molecular ions are currently of great interest [1–4]. Many of the investigations of such systems have involved partially oxidized stacks of planar transition metal complexes in which the metals are arranged in infinite chains. These systems include the tetracyanoplatinates (KCP) [5], metallophthalocyanines ($MPcI_x$) [6], metallotetrabenzoporphyrins ($M(OMTBP)I_x$) [7], and metallodiphenylglyoximates ($M(dpg)I_x$) [8, 9]. We report here a new conductive solid exhibiting anisotropic electrical behavior which may result from a unique type of interaction between molecules in the crystal.

The metallic complex 6,13-diacetyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenenickel(II), DADMTANi [10], was found to crystallize in two different morphologies depending on the solvent used for recrystallization. When using methanol or xylene as previously reported [10], red microcrystals A were obtained; using chloroform, copper-colored crystals B were obtained which had a mica-like structure consisting of loosely stacked layers. Although fragile, these crystals could be grown with dimensions as large as $50 \times 10 \times 1$ mm. Since these crystals possessed anisotropic optical properties with a metallic luster and high reflectivity, we undertook an investigation to elucidate their properties, particularly the electrical conductivity.

Elemental analyses indicated that both crystallographic forms A and B had identical chemical compositions (*Anal.* Calcd. for: $C_{16}H_{22}O_2N_4Ni$; C, 53.22; H, 6.14; N, 15.51; O, 8.86. Found (*A*): C, 53.27; H, 6.03; N, 15.66. Found (*B*): C, 53.43; H, 6.07; N, 16.06; O, 8.78). The oxygen analytical result for form B ruled out the inclusion of H_2O or alcohol as the cause for the differences observed in their properties. Additionally, solution properties

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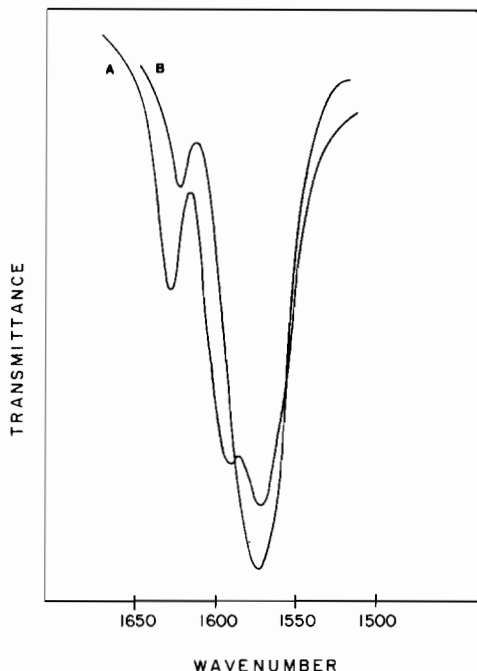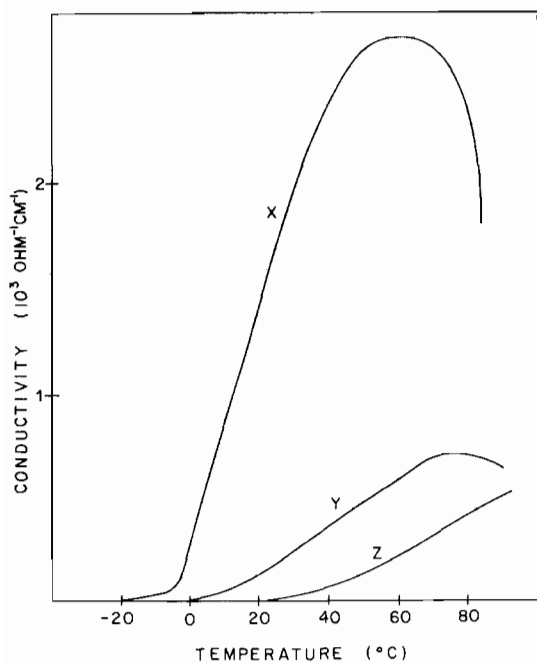
Fig. 1. Infrared spectra of the two crystallographic forms of DADMTANi(II). (A) -red crystals, form A; (b) metallic-looking crystals, form B.

of forms A and B were the same. The physical properties of the two solid forms, however, were different. Comparison of the X-ray powder patterns of the crystallographic forms indicated two different crystal packing morphologies. Also, high resolution IR spectra of forms A and B showed a marked difference in the 1650–1550 cm^{-1} region (Fig. 1). Three bands were present for the red crystals A, while only two absorptions were observed for the metallic-looking crystals B.

Four probe pressed powder conductivity measurements were carried out on the two types of crystals. The red crystals A had a low conductivity, less than 10^{-11} ohm^{-1} cm^{-1}; the metallic-looking crystals B had a conductivity of *ca.* 10^{-8} ohm^{-1} cm^{-1}. Two probe single crystal conductivity measurements were carried out only on crystals of form B, since no crystals of form A suitable for these measurements could be grown. To make the measurements, the crystals were mounted across two Pt electrodes with a conducting graphite cement (Electrodag 502). The entire sample could be placed in a Schlenk tube and evacuated by a vacuum line to obtain data either under vacuum or an inert atmosphere.

The electrical conductivity of B was anisotropic with a value of 10^{-6} ohm^{-1} cm^{-1} along the crystal dimension of maximum conductivity. Upon exposure to iodine vapor, the copper-colored crystals

Fig. 2. Typical temperature dependence of the electrical conductivity along three orthogonal crystal dimensions.

Fig. 3. Proposed polymeric structure of DADMTANi(II).

B turned black and the conductivity increased typically by *ca.* 10^5. This conductivity was again found to be anisotropic with the greatest value still along the major dimension of the crystal. During iodination, the conductivity increased with time until it reached a limiting maximum value. The time for complete iodination depended on the crystal size (*e.g.*, a 5.7 X 2.1 X 0.8 mm crystal reached a constant conductivity in *ca.* 20 h). The iodinated crystal appeared to be uniformly blackened throughout and to have increased in size by *ca.* 10%. This interaction with iodine was not reversible; evacuation of the iodinated crystals for 24 h did not result in any changes in the conductivity. Also, the iodinated from B was stable on exposure to the atmosphere.

The temperature dependence of the electrical conductivity (σ) along the three different dimensions of the crystal is shown in Fig. 2. The temperature range for measuring the conductivity was from 200 K to 370 K. At the high end of this temperature range some decomposition appeared to take place. As the temperature was lowered from 370 K to 340 K the conductivity of the sample slowly increased showing metallic behavior. At about 340 K the conductivity reached a maximum, and upon further cooling, a slow transition occurred resulting in semiconducting behavior. The decrease in conductivity below this transition region is in an activated manner which is characteristic of semiconductors. The
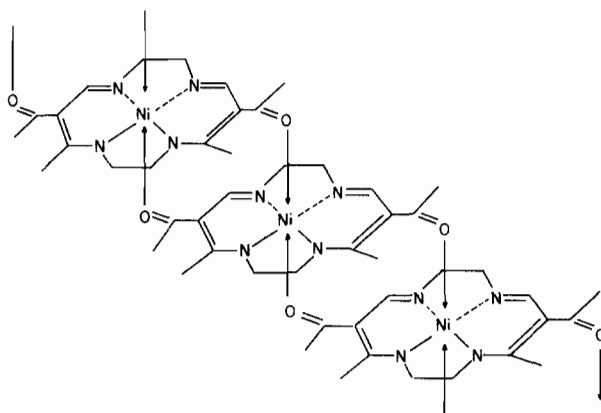
maximum values of the conductivity varied slightly from sample to sample which can be attributed to varying quality of the crystals. The observed conductive behavior is characteristic of low dimensional systems having a single conducting path. Similar relationships for σ *vs.* T have been reported for $M(OMTBP)I_x$ [7], KCP [11] and other systems [6a–12].

The differences in the properties of crystal forms A and B are most likely related to interactions associated with the differences in their solid state structures. For the red form A the IR data suggest that one of the acetyl CO's is free (1590 cm^{-1}), by comparison of its position with that of the free ligand, but that the other band (1575 cm^{-1}) is indicative of a CO which is interacting with a Ni site on an adjacent complex. The formation of discrete dimers can be envisioned having both free and bound CO's such that no long range communication exists between separate dimers. The metallic-looking form B, which does not possess a free CO stretch in the IR is proposed to have a polymeric chain structure as indicated in Fig. 3. In this case, portions of the macrocyclic π-frameworks would overlap although nonbonding interactions would be expected to be large. Such a polymeric structure has previously been suggested [13] for a similar Cu complex possessing acetyl CO's located on a ligand *trans* to each other. It should be noted, however, that stacked Ni complexes have been structurally characterized [14] for systems without ring acetyl groups and such an arrangement cannot be completely dismissed for our system.

As in other systems, the electrical conductivity of DADMTANi becomes appreciable when the crystal is exposed to molecular iodine. The irreversibility of this interaction, however, is not characteristic of other systems and suggests that the metallic-looking form B is not being doped in the same manner as has been observed for other related cases

[6–9]. The ring or metal could be oxidized; oxidation of the ring would result in a more planar conformation [14] possibly allowing closer intermolecular contact and larger conductivities. Experiments are presently in progress to resolve these questions. They include X-ray structural characterization and EPR and resonance raman spectroscopy.

In conclusion, we have found another example of a conductive molecular solid having anisotropic electrical properties. This may be the prototype for a new class of low dimensional systems based on a unique interaction between adjacent molecules which can be advantageously employed to provide structural integrity to the stacked molecules.

Acknowledgment

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