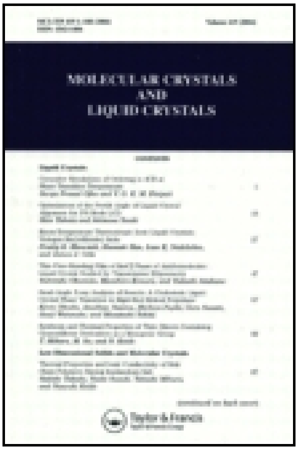

Molecular Crystals and Liquid Crystals

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Metallic Conductivity and Magnetic Interactions in Nickel and Copper Phthalocyanine Iodides

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METALLIC CONDUCTIVITY AND MAGNETIC INTERACTIONS IN NICKEL AND COPPER PHTHALOCYANINE IODIDES

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Abstract We discuss the charge transport and magnetic properties of the titled molecular metals. Replacement of the diamagnetic Ni(+2) by paramagnetic Cu(+2) introduces a novel coupling between local Cu(+2) spins the mobile charge carriers, and produces a coupled transition at 8 K.

INTRODUCTION

We are engaged in the synthesis of highly conducting molecular crystals through partial oxidation of porphyrin and phthalocyanine metal complexes. The chemical variability of porphyrinic metallomacrocycles, M(L), makes these complexes uniquely well suited for the exploration of the relationships between molecular and solid state transport properties, and offers the potential for chemically controlling the crystal structure and properties of new molecular conductors.[1]

Partial oxidation of M(L) complexes by molecular I_2 has produced a large number of new, quasi one-dimensional molecular metals.[1] In each case the crystal topology permits the strong intermolecular interactions required for high conductivity, and the structure is comprised of metallomacrocycle stacks surrounded by channels containing linear chains of iodine in the form of I_3^{-1} ions (Figure 1).[1]

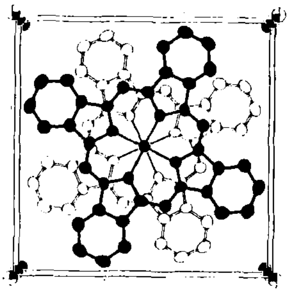

FIGURE 1. View down the c axis of the unit cell of Ni(pc)I and Cu(pc)I. Hydrogen atoms have been omitted for clarity.

As a demonstration of the unique chemical flexibility of these systems, we discuss nickel phthalocyanine iodide, Ni(pc)I, the first low-temperature molecular metal based on metal complexes, and Cu(pc)I which displays novel interactions between localized Cu(+2) spins and mobile charge carriers.

RESULTS

The charge carriers of Ni(pc)I are associated with π-molecular orbitals of the ring and the conductivity at room temperature has a value,[1] $\sigma \sim 500\ \Omega^{-1}\ \mathrm{cm}^{-1}$. This compound is the first based on a metal-organic complex that remains highly conducting down to the lowest available temperature, 100 mK (Figure 2),[2,3] and is the first to do so without the benefit of strong, chalcogen mediated interstack interactions. The conductivity maximum of ca. 20-30 K appears to be an extrinsic property, since the static susceptibility, which is temperature independent down to 2 K, thermopower, and epr all confirm that Ni(Pc)I is truly metallic down to 2 K and below.[3]

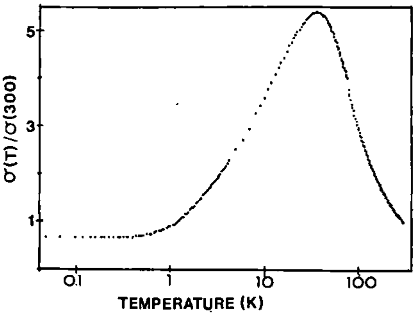

FIGURE 2. Representative plot of σ(T)/σ(300) for Ni(pc)I, where σ(300) ~ 500 Ω^{-1} cm^{-1}.

The absence of an observable metal-insulator transition is surprising. In general, when the physical properties of a molecular metal are dominated by strong unidimensional interactions, the compound exhibits a metal-nonmetal transition, most often of the Peierls type. The extremely narrow epr lines and weak magnetoresistance of Ni(pc)I suggest it to be highly one-dimensional,[3] as expected from the crystal architecture (Figure 1). Moreover, the closest non-hydrogen interchain contacts are between carbons separated by 3.70 Å in the plane of a Ni(pc) unit, and by 3.61 Å between a molecule in one stack and its neighbors either one unit (c/2) up or down in the adjacent stack. These distances are too long for appreciable interstack interactions. In short, Ni(pc)I appears to avoid a Peierls transition despite being quite strongly one-dimensional. Some of the possible explanations are discussed elsewhere.[3]

Metal variation in the highly conducting M(L)I provides a means of exploring the charge transport mechanism that is unique to the conductors based on metallomacrocyles. We have prepared single crystals of Cu(pc)I that have the same structure as Ni(pc)I and are even more highly conducting: $\sigma(300°C) \sim 1000\ \Omega^{-1}\ cm^{-1}$, and $\sigma(T)$ increases down to 20 K, the lowest temperature yet examined. Our initial magnetic measurements show that oxidation is ligand based; the open-shell divalent metal retains its paramagnetic ($S = \frac{1}{2}$) Cu(+2) oxidation state. The novel feature of Cu(pc)I is that it includes a dense (1/site) system of interacting, Cu^{+2} ($S = \frac{1}{2}$) local spins in addition to the "Fermi sea" of itinerant carriers that, like those of Ni(pc)I, are associated with π-molecular orbitals of the ring.

The copper ion's magnetic moment is a probe that interacts with, and provides information about the π-carrier spins. Preliminary epr studies show a single line whose g-value is temperature dependent. This result indicates a strong exchange coupling between Curie-like local spins and Pauli-like itinerant spins; in the terminology associated with the epr of local moments in atomic metals, the strongly bottlenecked regime obtains.[4] Strong exchange coupling between Cu(+2), with $\theta \sim 5$ K, further suggests indirect couplings of the local Cu^{+2} spins via the carriers, as well as dipole-dipole interactions and direct exchange. This may be schematized as in Figure 3.

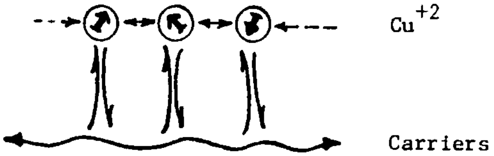

FIGURE 3

Analysis of the magnetic properties of Cu(pc)I should give us a deep insight into the charge transport process underlying the metal-like conductivity of this compound and, by inference, of other M(L)I as well.

Perhaps most interesting, we find that the epr signal of Cu(pc)I broadens and vanishes at ca. 8 K, in a transition whose breadth is less than 1 K (Figure 4).

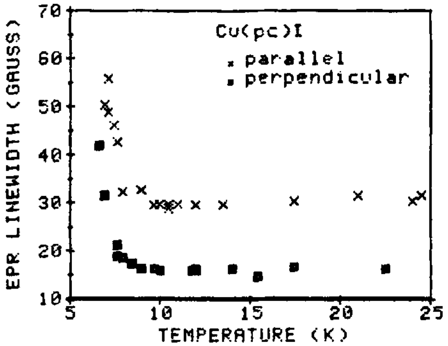

FIGURE 4. EPR linewidth of Cu(pc)I parallel and perpendicular to the stacking axis.

Susceptibility, nmr, and experiments are being undertaken to fully characterize this transition. However, since the epr signal is associated with the coupled magnetizations of the local and mobile spins, the epr result suggests the occurrence of a novel transition, perhaps to a spin-density wave state, that involves both spin systems.

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