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EFFECTS OF IODINATION ON THE ELECTRICAL CONDUCTIVITY
OF HYDROGEN BIS(PHTHALOCYANINATO) NEODYMIUM(III)

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Abstract Partial oxidation of hydrogen
bis(phthalocyaninato) neodymium(III) by molecular
iodine dramatically increases electrical
conductivity. The results are discussed in terms of
structural models.

INTRODUCTION

Iodination of metallomacrocycles has been shown to be an effective synthetic approach to low-dimensional conducting materials consisting of partially oxidized molecular stacks.¹ The weakness of this approach is that there is little synthetic control over the the small differences in molecular and lattice forces which control the formation of stacks. An improvement to this approach was provided by the "face-to-face" orientation of macrocycles found in the $[M(Pc)O]_n$ materials.² In this paper we show that a similar orientational effect exists in the linear chain compound

* deceased

composed of stacked hydrogen bis(phthalocyaninato) neodymium(III) [bis(Pc)Nd(III)] sandwich molecules.

EXPERIMENTAL

Bis(Pc)Nd(III) was prepared and purified using previously described methods.³ Partial oxidation of bis(Pc)Nd(III) was carried out with molecular iodine to obtain molecular compositions of bis(Pc)Nd(III)I_x with $x = 1.3$ and 1.8 . All materials were air stable during the period of the measurements. A pressure of 10^7 Pa was used to compress the materials into pellets 5 mm in diameter and typically 0.5 - 1.0 mm thick. The van der Pauw technique⁴ utilizing four-probe conductivity measurements was used. The probes were attached to the pellets using silver paste contacts. Room-temperature resistivity values were measured for several days to check for any chemical reaction at the electrodes; none was observed. After high temperature measurements (>300 K), room temperature resistivity was checked again to ascertain whether decomposition had occurred; none was observed. Several runs were made on each sample to demonstrate reproducibility. All possible permutations of the voltage and current leads around the four-probe network were examined at high and low temperatures to assure legitimate use of the van der Pauw theorem. A typical D. C. current of 10^{-5} amps was used for variable-temperature data sets. Ohmic behavior was observed for all samples.

RESULTS

Variable-temperature resistivity data shown in Figure 1

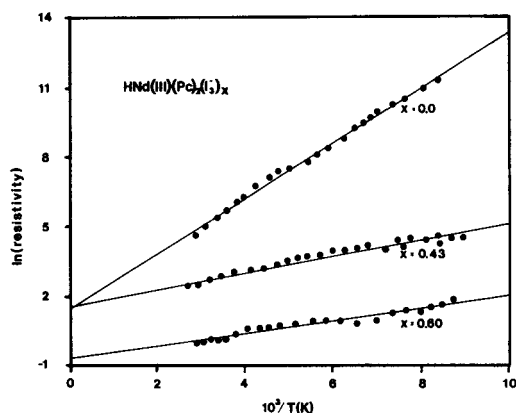


Figure 1. Electrical resistivity data for the series $\text{bis}(\text{Pc})\text{Nd}(\text{III})(\text{I}_3)_x$, with best-fit lines.

indicate the polycrystalline samples to be thermally activated semiconductors. The data were fit by least-squares techniques to the thermally-activated transport model

$$\sigma = \sigma_0 \exp(-\underline{\Delta}/kT) \quad (1)$$

where σ_0 is the infinite-temperature conductivity and $\underline{\Delta}$ is the apparent activation energy. The parameters which describe each of the samples are set out in Table I. The data for $\text{bis}(\text{Pc})\text{Nd}(\text{III})$ are in agreement with previously determined data⁵ (in ambient hydrogen and in air) which had revealed that absorbed oxygen decreased the resistivity values and the activation energies. Exposure of the iodinated complexes to oxygen was not expected to alter the

TABLE I Electrical conductivity parameters for the series $\text{bis}(\text{Pc})\text{Nd}(\text{III})\text{I}_x$.

x	$\sigma_o (\Omega^{-1} \text{cm}^{-1})$	$\sigma_{\text{RT}} (\Omega^{-1} \text{cm}^{-1})$	Δ (eV)
0.0(air)	0.24	4.5×10^{-3}	0.103
1.3	0.21	6.4×10^{-2}	0.030
1.8	1.95	0.8×10^{-1}	0.023

conductivity data since further oxidation was unlikely. Partial oxidation of $\text{bis}(\text{Pc})\text{Nd}(\text{III})$ by iodine dramatically reduces the resistivity and activation energy, as has been observed in the case of other metallomacrocycles.

DISCUSSION

The molecular structure of $\text{bis}(\text{Pc})\text{Nd}(\text{III})$ has been determined to be that of a sandwich compound,⁶ as opposed to the planar $\text{M}(\text{Pc})$ units found for first-row transition metal compounds. The neodymium ion occupies an eight-coordinate central position between two parallel but staggered (45°) phthalocyanine molecules (Figure 2). The eight neodymium-nitrogen bonds range from 2.39 to 2.49 Å. These molecular units pack into the crystal as a chain which has a herring bone motif. Location of the acidic hydrogen in the complex has been very elusive in terms of experimental verification. Nichol森, et. al.,⁷ proposed that the proton was firmly bound to only one of the phthalocyanine rings. To account for spectroscopic properties, Moskalev,

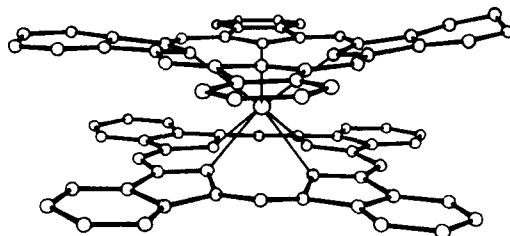


Figure 2. Sandwich structure of bis(Pc)Nd(III) .

et. al.⁸ suggested that the proton bridges bis(Pc)Nd(III) units in solution to form $\mu\text{-H}$ dimers, trimers, etc.. Electrochemical studies⁹ of solutions have shown that lanthanide sandwich compounds of the type discussed here show electrochromic properties which can be related to the oxidation state of the phthalocyanine rings. Hence, the presence of the acidic proton is of considerable importance in the redox properties of these systems. X-ray photoelectron spectra⁶ have shown that the eight nitrogens are chemically equivalent. These documented experiments lead to the conclusion that the proton is located between the bis(Pc)Nd(III) units in the solid state. Since the packing of the molecular units is similar to that of the β form of CuPc , this results in a "hydrogen bonding" bridged chain (Figure 3) qualitatively similar to the oxo-bridged M(Pc)O polymers.

In hydrogen atmosphere, bis(Pc)Nd(III) exhibits an activation energy that is 25% of that of CuPc and a room temperature resistivity that is four orders of magnitude smaller than that of CuPc . Measurements on bis(Pc)Nd(III)

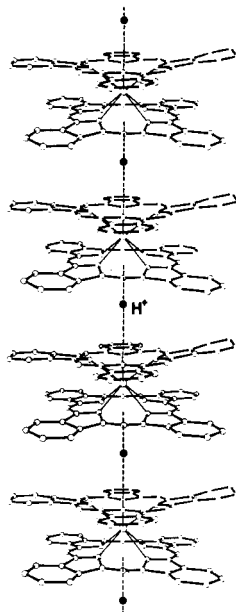


Figure 3. Hydrogen-bonded molecules in bis(Pc)Nd(III) forming a linear chain structure.

exposed to ambient air reveal decreased resistivity and activation energy relative to the same sample kept in a hydrogen atmosphere, presumably because of absorbed oxygen. The electrical conductivity values and activation energies for bis(Pc)Nd(III) are comparable to those of the Si(Pc)O polymer,² and bis(Pc)Nd(III) is a significantly better conductor than other M(Pc) systems. This can be understood in terms of the intermolecular hydrogen bond which promotes charge carrier transfer in a manner similar to that of the oxygen in the Si(Pc)O polymer. The presence of the acidic proton serves to bind the bis(Pc)Nd(III) units more tightly together, resulting in shorter intermolecular contacts than

those usually observed in $\text{M}(\text{Pc})$ systems. Hence, the increased conductivity and lowered activation energy can be understood in terms of the decreased distance between molecules and the consequential enhanced motion of the charge carriers.

The charge carriers in $\text{bis}(\text{Pc})\text{Nd}(\text{III})$ are mobile within the molecular units, and so we conclude that the conductivity of the system can be improved if the sandwiches are brought closer together. The effect of absorbed oxygen indicates that partial oxidation of the stacks increases the conductivity. Controlled oxidation of $\text{bis}(\text{Pc})\text{Nd}(\text{III})$ by iodine verifies that this model is plausible. Furthermore, on a simple electrostatic basis, it may be seen that the molecular sandwich units repel each other less when they have been partially oxidized. As a consequence, the distance between sandwich units decreases, the interaction between them increases, and a decreased activation energy and improved charge carrier transport results. $\text{Bis}(\text{Pc})\text{Nd}(\text{III})\text{I}_{1.3}$ has nearly the same infinite temperature conductivity as the unoxidized material, but only a slightly larger activation energy than the $x = 1.8$ material. The $x = 1.8$ material has the smallest activation energy, and its infinite temperature conductivity is larger than in the other two samples. These results indicate that the first oxidation level ($x = 1.3$) decreases the activation energy nearly to the minimum value possible in this structure, while oxidation to the $x = 1.8$ level only affects the number and the characteristics of the charge carriers.

It is well known that single crystal conductivities of low dimensional materials are usually two to three orders

of magnitude larger in the molecular stacking direction than in the pressed pellets of the same material. This is simply a consequence of the averaging of the crystallographic directions and interparticle resistance effects. Metallic conductivity behavior in the chain direction can be masked in the powder data, due to the insulating behavior perpendicular to the stacking direction. One should compare bis(Pc)Nd(III)I_y powder data to that of a pressed pellet of the molecular metal Ni(Pc)I_{1.0},¹⁰ which has $\sigma_{RT} = 7 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$ and $\Delta = 0.04$ eV. However, single crystal room temperature conductivities along the stacking direction of Ni(Pc)I_{1.0} are on the order of $6 \times 10^2 \Omega^{-1} \text{cm}^{-1}$ and are metallic according to variable temperature data. This suggests that the conductivity of the bis(Pc)Nd(III)I_y materials may very well be metallic in the chain direction, thus stimulating continued efforts to obtain single crystals. This research was supported in part by the Office of Naval Research.

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