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PREPARATION AND PROPERTIES OF SINGLE CRYSTALS OF HYDROGEN BIS(PHTHALOCYANINATO) NEODYMIUM(III)

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Abstract Single crystals of hydrogen bis(phthalocyaninato)neodymium(III) have been synthesized by electrochemical means. The crystals are semiconductors and follow Curie-Weiss behavior.

INTRODUCTION

Partially oxidized metallomacrocycles yield low-dimensional conducting materials. For example, $NiPcI_{1.0}$ (Pc = phthalocyanine) crystallizes with the formation of stacked, planar NiPc units and exhibits metal-like conductivity parallel to the stacking direction.[1] Lanthanide elements form sandwich-type compounds with phthalocyanine.[2] Pressed pellet samples of hydrogen bis(phthalocyaninato)neodymium(III), [bis(Pc)Nd(III)], and bis(Pc)Nd(III)I_y (y = 1.3 and 1.8) exhibit semi-conductive behavior with room temperature conductivities of 4.5×10^{-3}, 6.4×10^{-2} and $0.8 \times 10^{-1}\ \Omega^{-1}\ cm^{-1}$, respectively.[3] It has been reported that single crystals of $PcMPc_{ox}$ (M = lanthanide(III) and $Pc_{ox} = [C_{32}H_{16}N_8]^-$) can be obtained via electrochemical oxidation of the corresponding hydrogen bis(phthalocyaninato)M(III).[4] In this paper, we report the electrochemical synthesis, electrical conductivity, and magnetic behavior of single crystals of bis(Pc)Nd(III).

EXPERIMENTAL

The synthesis and purification of bis(Pc)Nd(III) was adopted from previously described methods.[5] The growth of single crystals was

achieved by electrochemical means similar to that reported for the preparation of $PcNdPc_{ox}$.[4] To 10 ml dimethylformamide and 0.1 ml hydrazine monohydrate was added 0.26 g bis(Pc)Nd(III). Upon filtration of the deep blue solution into an electrochemical cell fitted with a Pt wire (anode), graphite rod (auxillary electrode), and argon inlet and outlet tubes, a 0.150 V potential corresponding to an initial anodic current density equal to circa. 0.5 mA cm^{-2} was applied. After 48 hours, dark blue PcNdPc crystals were collected at the Pt wire and were also filtered from solution.

Four probe contacts were used for these preliminary conductivity measurements. Gold wire (0.1 mm diameter) leads were connected at both ends of the crystals with silver paste. A DC current of approximately 10^{-5} A was used for the variable temperature data sets. Temperatures were measured with a silicon diode. Ohmic behavior was observed for all samples.

Magnetic susceptibility data between 77 and 300 K were collected under helium using a Faraday balance fitted with a Cahn 2000 electronic balance. Calibration was accomplished with $Hg[Co(NCS)_4]$ and diamagnetic corrections, except for Nd(III), were made by using Pascal's constants. Temperatures were measured with a silicon diode.

RESULTS

Only the electrical conductivity along the long axis of each crystal, which presumably corresponds to the stacking direction of PcNdPc, was measured. The observed room temperature conductivities of three samples ranged from 0.008-0.04 Ω^{-1} cm^{-1} and variable temperature resistivity data indicated semi-conductive behavior. When $\ln\rho$ was plotted versus temperature, the low temperature (78-210 K) data were approximately linear and could be fit to the thermally activated transport model $\sigma = \sigma_o \exp(-/\backslash/kT)$

where σ_o is the infinite temperature conductivity, and Δ(0.031 eV per electron) is the energy of activation in this region. At temperatures greater than ~210 K, marked deviations from linearity occur. Most notably, between 210 and 260 K, a steep (~20 fold) rise in conductivity with increasing temperature was observed. Perhaps reminiscent of an exhaustive region of a semi-conductor, this peak was followed by a region (260-285°) in which conductivity significantly decreased with increasing temperature before the earlier temperature dependent behavior was resumed.

Magnetic susceptibility data for PcNdPc closely follows Curie-Weiss type behavior [$\chi = C/(T-\theta)$]. Using a non-linear least squares fitting routine, C and θ were calculated to be 1.64 and −4.93 K respectively. The magnetic moment of 3.61 μ_B at 300 K is close to the value of 3.62 μ_B expected for a Nd(III) species. The values of μ_{eff} showed only a minor dependence on temperature; at 80 K μ_{eff} is 3.52 μ_B.

DISCUSSION

Utilizing the synthetic scheme described above, Moskalev et. al.[4] reported the isolation of crystalline $PcNdPc_{ox}$. The reaction was assumed to involve the removal of an electron from the π-orbital of one phthalocyanine ring. In our hands, however, crystals of HPcNdPc were obtained instead. While exhibiting very similar infrared absorbances (874, 1053, 1108, 1213, 1351, and 1438 cm^{-1}) and lattice parameters (tetragonal; a = 13.85 Å, c = 6.62 Å) to those reported for the oxidized complex, the magnetic susceptibility measurements (μ_{eff} = 3.61 μ_B) are consistent only with the presence of Nd(III); no further contribution from a Pc_{ox}^{1-} species was observed.

Although single crystals of hydrogen bis(phthalocyaninato) Nd(III) display increased conductivities relative to pressed pellet samples, only semi-conductive behavior was observed.

However, partial oxidation of these crystals is expected to increase the electrical conductivity and perhaps make it metallic. Pressed pellet samples of bis(Pc)Nd(III)I_y exhibit an 18-fold increase in conductivity on going from y = 0 to y = 1.8.[3] Likewise, samples (y = 0) exposed to oxygen display conductivities greater than those kept under hydrogen.[6] The effect of partial oxidation should be even more pronounced in single crystals where full advantage of the one-dimensional stacks can be taken. In this light, it may be noted that $NiPcI_{1.0}$ is metallic only in crystalline form.[1] Reflective single crystals of iodinated bis(PC)Nd(III) have been obtained and are currently being studied.

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