I, we have listed the ratio of the coefficient of the diffuse d orbital to that of the contracted d orbital. For all three orbitals the formamidato species has a higher ratio. Therefore, the d orbitals are expanding more in the formamidato species due to donation from the nitrogen, which leads to better overlap and a stronger quadruple bond.

We will be reporting potential-energy curves for these two compounds as well as calculations on other quadruply bonded dichromium systems in a forthcoming paper. Preliminary results predict an equilibrium bond distance of 2.4 Å for tetrakis(formato)dichromium.

These results indicate that the nature of the bridging ligand strongly affects the strength of the quadruple bond. Thus, the inductive effect of the bridging ligand may determine whether or not axial ligands will bond. It is likely that on species with four carboxylato ligands, the Cr atoms cannot compensate for the loss of electron density when the axial ligands are removed like they can in compounds with very short Cr–Cr quadruple bonds. This is perhaps why the tetrakis(carboxylato) species attract axial ligands so strongly. These results do not mean that the presence of axial ligands is unimportant but that the inductive effects of the bridging ligands are equally important. Thus, if a tetrakis(carboxylato) species without any axial ligands could be synthesized, there might be a decrease in the quadruple bond length, but not enough to move it into the group of compounds with bond lengths less than 1.90 Å.

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Registry No. Cr, 7440-47-3; tetraformatodichromium, 63448-51-1; tetraformamidatodichromium, 84237-52-5.

Low-Temperature Metallic Conductivity in a Metallomacrocyclic Crystal: Nickel Phthalocyanine Iodide

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Only a few molecular crystals exhibit high electrical conductivity down to low temperature,[1-5] and only one has been reported to superconduct at ambient pressure.[6] These few known compounds (Table I) are based on derivatives of organic chalcogenides, and the low-temperature conducting state is stabilized through two- or three-dimensional, chalcogen (S or Se) mediated, interstack interactions. We report here that nickel phthalocyanine iodide, NiPcI,[7] which we earlier found to exhibit metal-like conductivity at temperatures above ca. 50 K,[8] is the first molecular crystal that behaves as a metal down to the lowest available temperature, 100 mK, yet contains neither chalcogen-mediated nor indeed any apparent strong interstack interactions. In addition, it is the first low-temperature molecular metal based on a metal-organic complex.[9]

Table I. Low-Temperature Molecular Conductors

compound[a]	σ(room temp), Ω^{-1} cm^{-1}	T_L, K[b]	$\sigma(T_L)/\sigma$(room temp)	ref
Ni(Pc)I	~550	0.1	0.5-2	8
HMTSeF-TCNQ	2×10^3	1.1	0.5	2
$(TSeT)_2X$[c]	2×10^3	4.2	~1	c
$(TMTSeF)_2ClO_4$	~10^3	1.4[d]	∞[d]	6
$(BEDT\text{-}TTF)_2ClO_4$	260	1.4	~35	5

[a] See ref 7 for abbreviations. [b] Lowest temperature examined, except as noted. [c] X = Cl;[3] X = Br;[3] X = I.[4] [d] Superconductive transition, 1.4 K.

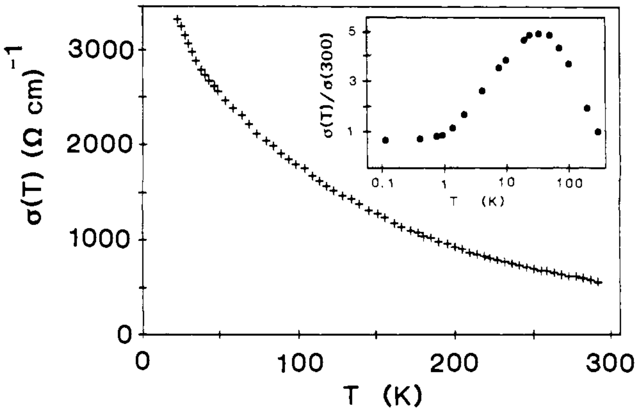

Figure 1. Temperature response to the needle-axis (*c*-axis) conductivity of a NiPcI crystal. Inset: temperature response to the needle-axis conductivity emphasizing the low-temperature behavior; the conductivity has been normalized to the ambient-temperature value of ca. 600 Ω^{-1} cm^{-1}.

The NiPcI crystals (~2 × 0.03 × 0.03 mm) were obtained and EPR measurements carried out as reported previously.[8] Single-crystal conductivity data from 300 to 20 K were obtained by a four-probe ac phase-locked technique described elsewhere.[10] Resistivity measurements down to a temperature of 100 mK as well as magnetoresistance and thermoelectric power measurements were done on previously described apparatus.[11] The crystals were mounted with a conducting palladium paste on thin (8 μm) graphite fibers (Alfa/Ventron) that had been chemically silvered.[10]

The needle (stacking) axis room-temperature conductivity, $\sigma_{\parallel}$, of NiPcI crystals has an average value of ca. 550 Ω^{-1} cm^{-1} and invariably increases with cooling.[8] At low temperature, the four-probe measurements were very crystal dependent, and we ascribed spurious conductivity "transitions" to stress from the relatively thick contact wires; NiPcI crystals are very brittle when cold. A single four-probe measurement and a single, very preliminary, high-frequency contactless measurement coincided in giving a reversible conductivity maximum at 55 K, and therefore we concluded that at about this temperature there was a reversible transition to a state of lowered conductivity. However, upon cooling Ni(Pc)I crystals mounted relatively free of stress through

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use of the thin silvered graphite fibers, we now find the conductivity typically continues to increase well below 50 K, as shown in a data set terminating at ca. 20 K (Figure 1) and then reaches a gentle maximum having $\sigma(T_m) \sim 2000\text{–}5000\ \Omega^{-1}\ \text{cm}^{-1}$ at $T_m \lesssim 25$ K (Figure 1, inset). Both T_m and the relative conductivity show some variability with crystal, part of which undoubtedly reflects crystal quality and probably also residual stress in the mounts.[12] Upon further cooling, the conductivity at first decreases gradually, but it does not become vanishingly small as in most molecular crystals. Instead, it levels off to a high asymptotic ($T \rightarrow 0$) value (Figure 1, inset) that varies from about $^1/_2$ to 2 times that at room temperature. For comparison (Table I), the asymptotic low temperature to ambient conductivity ratio for the first low-temperature molecular conductor, HMTSeF-TCNQ,[2] is $\sigma(1.1)/\sigma(\text{room temp}) \sim {}^1/_2$.

The NiPcI charge carriers are associated with delocalized π orbitals on the macrocycle, with an additional small spin density ($\lesssim 0.5\%$) on iodine,[8] and have a narrow line width at room temperature ($\Gamma_{\parallel} = 2.4$ G, $\Gamma_{\perp} = 2.0$ G) that decreases upon cooling. In contrast, among the other molecular crystals that remain highly conducting at the lowest temperatures, scattering processes associated with two or three dimensionality cause the EPR line to be broad (e.g., $(\text{TMTSeF})_2\text{ClO}_4$),[13] even unobservably so (e.g., HMTSeF-TCNQ).[14] The spin susceptibility of NiPcI is metal-like, being virtually temperature independent down to the lowest accessible temperature, 2 K.[10b] The thermoelectric power of NiPcI single crystals is positive, confirming the hole conduction mechanism expected for the oxidized NiPc stacks, and varies linearly with temperature with a nearly zero intercept, consistent with metallic behavior down to the lowest measured temperature of $\sim$10 K.[15] Fitting the data yields a tight-binding bandwidth of $4t \sim 0.44$ eV, in good agreement with $4t = 0.37$ eV, deduced from the susceptibility.[8]

The temperature-independent susceptibility, the thermoelectric power proportional to temperature, and the high conductivity as $T \rightarrow 0$ K are all precisely as expected if NiPcI is a truly metallic conductor. In addition, the weak interstack contacts, the narrow EPR line width, and a weak magnetoresistance[16] indicate that the carriers are strongly one dimensional. However, upon cooling, a conductive one-dimensional system normally is expected to undergo a metal–insulator transition[1] that is correlated with a periodic (Peierls) distortion (in this case in the conducting NiPc stack).[17] This in turn would lead to a vanishingly small conductivity as $T \rightarrow 0$, contrary to observation. The conductivity maximum at T_m perhaps reflects a tendency of NiPcI to undergo a metal–insulator phase transition that is suppressed by the disorder potential from the iodine chains. Disorder might produce a sufficient number of states at the Fermi level to give a metallic-like temperature variation of the susceptibility and thermoelectric power yet cause the conductivity to have a quasi-metallic behavior at low temperature. Intermolecular forces between the large NiPcI metallomacrocycles might also introduce geometric constraints not operative in the conductive crystals prepared from smaller building blocks (Table I) and may play a part, along with the disorder in the triiodide chains, in stabilizing the NiPcI metallic state. In any event, the present results pose new questions and present new opportunities in the study of charge transport in molecular crystals.

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$$S = \left(\frac{-\pi^2 k_B{}^2}{6|e|t} \frac{\cos(\pi\nu/2)}{\sin^2(\pi\nu/2)} \right) T$$

where t is the transfer integral and $\nu = 2 - \rho$ is the number of conduction electrons per molecule (1.67). See: Khanna, S. K.; Yen, S. P. S.; Samoano, R. B.; Chaikin, P. M.; Ma, C. L.; Williams, R.; Samson, S. *Phys. Rev. B* **1979**, *19*, 655–663.

(16) Magnetoresistance measurements on NiPcI performed at 4.2 K showed a positive $\Delta\rho/\rho$ of order 5% in a 50-kG field. Thus NiPcI is similar to HMTSeF-TCNQ, which has no detectable magnetoresistance above 100 K but does have a modest positive effect ($\Delta\rho/\rho \simeq 3\%$ at 28 kG) at 4.2 K. See: Cooper, J. R.; Weger, M.; Jerome, D.; Lefur, D.; Bechgaard, K.; Bloch, A. N.; Cowan, D. O. *Solid State Commun.* **1976**, *19*, 749–754.

(17) We note that a possible trimerization of the NiPc stacks in response to the trimerization of iodine to form I_3^- is not a Peierl's distortion, does not cause a gap at the Fermi surface, ($k_F = 5\pi/6a$, where a is the interplanar spacing, for $\rho = 0.33$) and should not lead to a metal-to-insulator transition.

Resonance Raman Excitation of O_2 Stretching Vibrations of Oxy(tetraphenylporphinato)cobalt(II) at 457.9 nm

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The intense current interest in dioxygen adducts of metalloporphyrins stems from their obvious importance to the study of biological oxygen carriers and heme-containing oxidoreductases as well as their relevance to recent investigations of metalloporphyrin-based oxidation catalysts.[1-3] For this reason, it is essential to develop and demonstrate readily accessible and effective probes for characterization of these important adducts.

The O_2 stretching ($\nu(O_2)$) vibrations of dioxygen adducts of metal complexes provide valuable information about the nature of the metal–O_2 bond (superoxo/peroxo) and the geometry of the metal–O_2 moiety (end on/side on). The $\nu(O_2)$ of Co(II) Schiff base complexes can be resonance enhanced by laser lines in the visible region because their Co(II)–O_2 charge-transfer (CT) bands are located in the 500–600-nm region.[4-6] In contrast, resonance enhancement of $\nu(O_2)$ of Co(II) porphyrins by "visible" laser lines (450–700 nm) has not been observed[7,8] since their Co(II)–O_2 CT bands are in the UV region. Only recently, Tsubaki and Yu[9] were able to observe the $\nu(O_2)$ of oxycobalt myoglobin and oxycobalt hemoglobin by usng the 406.7-nm line of a Krypton ion laser. In this communication, we show that the $\nu(O_2)$ of a Co(II) porphyrin, Co(TPP)(py)O_2, can be observed by using the 457.9-nm line of a conventional argon ion laser if proper experimental conditions are met.

As is well-known,[6] the concentration of the 1:1 O_2/Co adduct in solution equilibria increases as the temperature is lowered and

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