Table I. The Amounts of Various Metal Salts Which Become Bound to Polymer **1** in Tetrahydrofuran

Metal salt	Quantity bound (mequiv of metal/g of polymer)
$Cr(NO_3)_3$	0.22
MnI_2	0.14
$FeCl_3$	0.83
$RuCl_3$	Not determined
$CoCl_2$	0.35
$Ni(NO_3)_2$	0.70
$Pd(O_2CCH_3)_2$	0.73[a]
$CuBr_2$	0.34 and 0.37[b]
$AgNO_3$	Not determined

[a] Determined by elemental analysis for Pd (Spang Microanalytical Laboratory). [b] Two different batches of polymer were used.

Table II. Effect of Solvent on the Quantity of $FeCl_3$ Bound to **1**

Solvent	Swelling factor[a]	Quantity bound (mequiv/g)
Methanol	1.0	0.002
Acetonitrile	1.4	0.25
Tetrahydrofuran	2.2	0.83
Ethyl acetate	2.4	1.2
Ethyl acetate-Benzene (1:1)	3.2	1.2

[a] The ratio of volume of swollen to nonswollen polymer **1**.

weak, broad band at ~1700 cm^{-1} and by an increased intensity of the bands at 1100 and 905 relative to the intensity of those at 700 and 755 cm^{-1}.

The data in Table II show that the amount of iron bound to the polymer can be controlled, at least in part, by proper choice of the solvent system. Only binding to surface bipyridyl groups should occur in methanol. The amount of iron binding increases as the swelling factor increases, to a maximum at ethyl acetate. The lack of further increase in the extent of iron incorporation may indicate that all the bipyridyl sites are now complexed.

The potential applications of **1** and its metal complexes should be obvious and the catalytic and analytical properties of these materials are currently under vigorous study.

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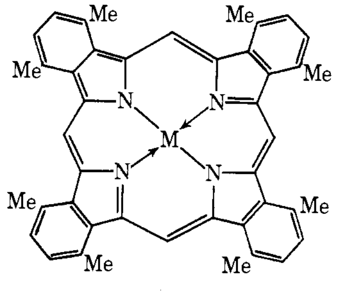
Conductive Molecular Crystals. Partially Oxidized Octamethyltetrabenzporphyrins

Sir:

The study of the quasi-one-dimensional electrical and magnetic properties of stacked molecular crystals is currently of great experimental and theoretical interest,[1] but the range of materials with high conductivities remain limited. It appears that two necessary conditions for obtaining high electrical conductivity are a structure containing infinite stacks of closely packed planar molecules and the occurrence of a nonintegral formal oxidation of the constituents. Guided by these requirements we have embarked on a program of synthesizing nonintegral oxidation-state crystals through substoichiometric oxidation of planar macrocyclic transition ion complexes (ML).

The I_2 oxidation of the metallophthalocyanines (M(Pc)) has recently been shown to yield highly conductive materials.[2] As part of the program to explore metal-macrocycle systems, we have prepared a variety of transition-metal complexes of 1,4,5,8,9,12,13,16-octamethyltetrabenzporphyrin



M(OMTBP)

(M(OMTBP)) and have subjected them to I_2 oxidation forming the partially oxidized $M(OMTBP)(I)_x$. In this communication we discuss the oxidation products of Ni(OMTBP), for which single crystals of suitable quality for characterization have been obtained. A particularly important result is the isolation of conductive single crystals with two distinct degrees of partial oxidation, both of which exhibit metal-like conductivity.

The condensation reaction[3] of 1,3,4,7-tetramethylisoindole[4] and nickel acetate tetrahydrate directly gives Ni(OMTBP), which was purified by recrystallization from 1,2,4-trichlorobenzene. The parent macrocycle and I_2 give Ni(OMTBP)(I)$_x$ by a diffusion technique. Two materials are obtained, usually as mixture of crystals, which may be physically separated on the basis of color and shape. Depending on the growth conditions, the percentage of each can vary. As determined by carbon, hydrogen, and nitrogen elemental analysis, the two materials correspond to two stoichiometries, $x = 1.05 \pm 0.1$ and $x = 2.9 \pm 0.3$.[5] Resonance raman spectra were taken on microcrystalline samples of both the $x = 1.05$ and $x = 2.9$ complexes, with an excitation wavelength of 5145 Å. Resonance absorptions were seen at 104, 213, and 320 cm^{-1}, characteristic of a symmetrical I_3^-[6], with no peaks observed for I_2. Based on the previous studies,[2,7] this result suggests that the proper formulation for these complexes should therefore be Ni(OMTBP)$(I_3^-)_y$, with $y = 0.35 \pm 0.03$ and $y = 0.97 \pm 0.10$.[8] The macrocycle oxidation state (ρ) is then equal to y and the former complex, at least, exhibits the desired nonintegral oxidation state, and the same may be true of the latter.

X-ray structure studies[9] of Ni(OMTBP)$(I_3)_{0.35}$ show that the crystal is tetragonal with the macrocycle stacked in infinite columns, at a separation of $\frac{1}{2}c = 3.778$ Å; the format is similar to that observed for Ni(Pc)$(I_3)_{0.33}$, but the distance between Ni(OMTBP) macrocycles is substantially greater than between the Ni(Pc)(3.24 Å).[10] Because presently available crystals of Ni(OMTBP)$(I_3)_{0.97}$ are extremely small, x-ray crystallographic measurements on this material have not yet been made.

The relationship between physical properties and degree of partial oxidation in conductive quasi-one-dimensional materials is a matter of keen interest, and this highlights the present isolation of two materials with different values of ρ. Crystals of organic donors or acceptors which differ in their average degrees of electron occupancy are known;[1] most notable perhaps is the range of compositions of the tetrathiofulvalene (TTF) halides.[11] In contrast, the previously observed conductive metal-containing molecular crystals, such as $K_2Pt(CN)_4Br_{0.3}\cdot 5H_2O$ (KCP), all exhibit a partial oxidation of $\rho = \frac{1}{3}$, within narrow limits.[1,12] The compounds Ni(Pc)$(I_3^-)_{0.33}$ and Ni(OMTBP)$(I_3^-)_{0.35}$ appear to be analogous to the previously studied metal-containing systems; this in turn would suggest that the isolation of Ni(OMTBP)$(I_3^-)_{0.97}$ represents a real novelty. However, for both the $y = 0.35$ and $y = 0.97$ materials, single-crystal EPR studies at room temperature reveal a single narrow line ($W_{pp} \sim 5$ (G) with $g_\parallel = 2.012$ located along the molecular normal (stacking directions) and $g_\perp = 2.006$. These values are free-radical like, and quite different from those expected for oxidation at the nickel ($g_\perp \sim 2.2$, $g_\parallel \sim 2.0$).[13] This indicates that the hole states are those of a π-cation radical and largely macrocycle based, with minimum spin density on Ni. Thus, it rather appears that these systems are similar to the organic "molecular metals", rather than to KCP and its analogues, with the metal ion acting as an "internal substituent" to the macrocycle. Since no conductors based on tetracyanoquinodimethan (TCNQ) or TTF have yet been found with $\rho \sim \frac{1}{3}$, it therefore seems that the ready isolation of $\rho = \frac{1}{3}$ Ni(OMTBP) and Ni(Pc) crystals is the novelty.

Single-crystal electrical conductivities were measured by a four-probe, ac phase-locked technique[14] at 27 Hz. The Ni(OMTBP)$(I_3)_{0.35}$ crystals used were nominally 0.9 mm long with octagonal faces of ~0.02 mm in width. The Ni(OMTBP)$(I_3)_{0.97}$ crystals were generally 1.0 mm long by 0.005 mm wide. The electrical contacts were made with a palladium paint prepared locally. A constant excitation current of 10 μA root mean square was used throughout the measurements, after the voltage-current response was first found to be ohmic over the current range, $0.1\ \mu A \leq I \leq 10^3\ \mu A$.

The temperature response of the electrical conductivity along the chain axis ($\sigma_\parallel$) for both $y = 0.35$ and $y = 0.97$ materials is shown in Figure 1. As the temperature is lowered from 380 to 300 K, the conductivity of Ni(OMTBP)$(I_3)_{0.35}$ slowly increases, thus exhibiting a metal-like behavior. There is a broad maximum in conductivity ($\sigma_\parallel{}^m$) occurring near $T_m \sim 300$ K; upon a further decrease in temperature, down to the lower limit of the experiment at 45 K, the conductivity decreases in an activated manner, indicating the presence of an energy gap at the Fermi surface. The value of T_m is somewhat sample dependent, ranging from ~260-330 K and the corresponding $\sigma_\parallel{}^m$ is inversely related to T_m, ranging from 16 to 4 (Ω cm)$^{-1}$; these variations presumably reflect crystal quality. The observation of such a conductivity maximum is apparently characteristic of "metallic" behavior in quasi-one-dimensional systems with a single conducting stack, and analogous curves for $\sigma_\parallel$ vs. T are seen for KCP,[15] N-methylphenazinium (NMP)-TCNQ,[16] quinolinium (TCNQ)$_2$,[17] and the TTF halides[12] and pseudohalides.[18] Below T_m, the value of $\Delta(T) = d\ln\sigma/d(^1/_T)$ slowly increases with decreasing T and reaches a constant low-temperature value of $\Delta(0) \sim 45$ meV by ~160 K.

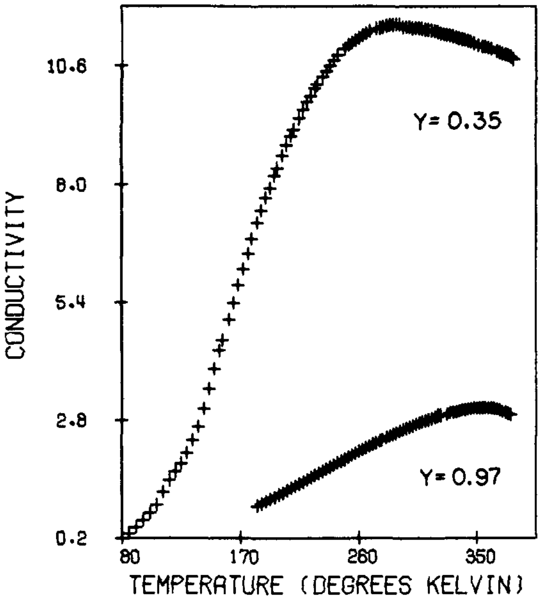


Figure 1. Plot of the conductivity (Ω^{-1} cm^{-1}), vs. temperature (K) for Ni(OMTBP)$(I_3^-)_y$, with $y = 0.35$ and $y = 0.97$, as indicated.

The conductivity at the maximum is ~15 (Ω cm)$^{-1}$, about an order of magnitude lower than for the other above-mentioned materials. However, the carrier mobility in all these materials is in fact rather similar. Within the framework of one-electron band theory, there is a simple relation between the electronic mean free path along a chain, λ, the conductivity σ, and the cross-sectional area per conducting stack, A:[19]

$$\sigma_\parallel = 2e^2\lambda/\pi\hbar A$$

Since A for Ni(OMTBP)$(I_3)_{0.35}$ is roughly 2.5-fold larger than for the other crystals, for equal values of λ a smaller value of $\sigma_\parallel$ must result. From observed values of σ and A, we find that λ for Ni(OMTBP)$(I_3)_{0.35}$ is only several times smaller than for NMP-TCNQ, Qn(TCNQ)$_2$, or KCP.[20] The conductivity of Ni(OMTBP)$(I_3)_{0.35}$ at room temperature is roughly 20-fold less than that for Ni(Pc)$(I_3)_{0.33}$,[10] but in this case there is no significant difference in A. Since the degree of partial oxidation is also the same, the diminished conductivity can thus be directly related to the increased intermolecular distance and the change in macrocycle, but the decrease seems to be surprisingly small, considering the large increase in intermolecular spacing.

The room temperature conductivity of Ni(OMTBP)$(I_3)_{0.97}$

is $\sigma_{\parallel} \sim 3.3$ $(\Omega\ \mathrm{cm})^{-1}$, only ~5-fold less than that of the $y = 0.35$ material. Near and below room temperature the conductivity is activated, also with an activation energy extrapolated to 0 K of $\Delta(0) \sim 50$ meV. Moreover, the qualitative shapes of the plots of $\sigma(T)$ are in fact quite similar for both compositions. As the temperature is increased above ambient, $\sigma_{\parallel}(T)$ for $\mathrm{Ni(OMTBP)(I_3)_{0.97}}$ also shows a broad conductivity maximum, but with $T_{\mathrm{m}} \sim 340$ K, roughly 40-60 K greater than T_{m} for the $y = 0.35$ phase. Again, for different $y = 0.97$ preparations, T_{m} will vary and $\sigma_{\parallel}{}^{\mathrm{m}}$ is inversely related to T_{m}.[21]

Both the room temperature value of $\sigma_{\parallel}$ and the shape of the $\sigma_{\parallel}(T)$ vs. T curve for $\mathrm{Ni(Pc)(I_3)_{0.33}}$ differ sharply[10] from the results for $\mathrm{Ni(OMTBP)(I_3)_{0.35}}$. This shows that apparently modest chemical variations in the macrocycle structure can substantially alter the physical characteristics of a partially oxidized ML system. In contrast, the differing degrees of oxidation for the two materials based on Ni(OMTBP) apparently lead rather to a quantitative difference in the response of $\sigma_{\parallel}$ vs. T. However, the change in properties with increased oxidation must reflect any structural alteration as well as the electronic difference. A fuller understanding of the dependence of conductivity on the degree of oxidation must thus await further studies and the complete crystal structure determinations.

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(21) We report the high-temperature behavior ($T \leq 370$ K) of the $y = 0.97$ composition with some caution, as the conductivity curve is not wholly reproduced upon cycling, suggesting the possibility of some crystal degradation and/or chemical reaction with the contacts. Observations of $\mathrm{I_2}$ loss indicate that these crystals are stable up to 380 K and possibly for 390 K, at least for ~0.5 h; $\mathrm{I_2}$ is lost at 400 K, yielding crystals whose appearance is is that of the $y = 0.35$ material.

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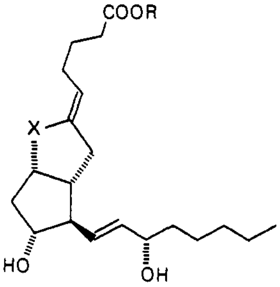
6,9-Thiaprostacyclin. A Stable and Biologically Potent Analogue of Prostacyclin ($\mathrm{PGI_2}$)

Sir:

The discovery of prostacyclin ($\mathrm{PGI_2}$, **1**)[1] late in 1976 has not only revolutionized current concepts in cardiovascular research[2] but has also thrust this molecule into the forefront of biological and chemical research.[3] Although several syntheses[4-6] have made it readily available, its unstable nature encumbers biological studies and makes it a doubtful pharmacological agent. In light of its biological importance, the synthesis of stable physiological mimics deserves a high priority. Even though some analogues of this molecule have been reported,[7] prostacyclin is at least two hundred times more potent than the most active of these substances.[8,9] In this communication we report the synthesis and preliminary biological properties of a potent and relatively stable analogue of prostacyclin ($\mathrm{PGI_2}$), namely 6,9-thiaprostacyclin (**2**).



1, X = O, R = H
2, X = S, R = H
3, X = S, R = $\mathrm{CH_3}$ or $\mathrm{C_2H_5}$

The methyl ester of 15-acetoxy $\mathrm{PGE_2}$ (**4**)[10] was converted to its tetrahydropyranyl ether (**5**)[11] with dihydropyran (1.5 equiv) under acid (*p*-toluenesulfonic acid) catalysis in methylene chloride at 25 °C (100% yield) and reduced with excess zinc borohydride (DME, 25 °C, 15 h) to afford the 9β-$\mathrm{PGF_{2\alpha}}$ derivative **6**, as the major product together with the 9α isomer (9β:9α ratio, 55:45) in 95% total yield. Chromatographic purification of **6** (silica; ether; 9β, R_f 0.47; 9α, R_f 0.59) followed by treatment with methanesulfonyl chloride (1.2 equiv) in methylene chloride at −20 °C in the presence of triethylamine led to the mesylate **7** (100%). When **7** was exposed to excess potassium thioacetate in dimethyl sulfoxide at 45 °C for 24 h the thioacetate **8** was formed in 90% yield. Removal of the tetrahydropyran protecting group with acetic acid–tetrahydrofuran-water (3:2:2) at 45 °C (20 h) resulted in the formation of diacetate **9** (98% yield), which, in turn, yielded 9-thio $\mathrm{PGF_{2\alpha}}$ methyl ester (**10**) upon treatment with anhydrous potassium carbonate (4 equiv) in absolute methanol at 25 °C (yield, 83%).

A second route to 9-thio $\mathrm{PGF_{2\alpha}}$ methyl ester (**10**), the first key intermediate for the synthesis of 6,9-thiaprostacyclin (**2**), was developed starting with the readily available 11,15-bis-(tetrahydropyranyl) ether $\mathrm{PGF_{2\alpha}}$ methyl ester (**11**).[12] This