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Structural, Magnetic, and Charge-Transport Properties of a New One-Dimensional Molecular Conductor, Ni(tprpc)$I_{1.67}$ (tprpc = 2,7,12,17-Tetrapropylporphycenato)

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Chemical oxidation of (2,7,12,17-tetrapropylporphycenato)nickel(II), Ni(tprpc), with iodine affords the new one-dimensional molecular conductor Ni(tprpc)$I_{1.67}$. The compound is composed of partially oxidized ($+^1/_3$) Ni(tprpc) cations packed in a slip-stack manner along the *b* axis. The stacks are surrounded by disordered chains of iodine, identified as I_5^- by Raman spectroscopy. The interplanar distance between Ni(tprpc) macrocycles is 3.306(10) Å, but the Ni–Ni distance is the *b* axis repeat distance, 4.982(1) Å. The conductivity measured along the needle (crystallographic *b*) axis of a single crystal is $2.5 \times 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at room temperature and may be fit to the expression $\sigma = \sigma_0 \exp(-\Delta E/k_BT)$ ($\sigma_0 \approx 1$, $\Delta E = 0.15(2)$ eV). EPR measurements confirm that the tprpc ligand is oxidized. The compound crystallizes in space group C_{2h}^6-$C2/c$ of the monoclinic system with four formula units ($C_{32}H_{36}I_{1.67}N_4Ni$) in a cell of $a = 22.548(5)$ Å, $b = 4.982(1)$ Å, $c = 27.156(5)$ Å, $\beta = 109.51(3)°$ ($V = 2875.4(10)$ Å^3) at 108 K. The structure has been refined on F^2 (2923 unique reflections) to $R_w(F_o^2) = 0.209$. The conventional agreement index $R(F)$ is 0.099 for the 1240 reflections having $F_o^2 > 2\sigma(F_o^2)$. The relatively high *R* index results from our inability to model adequately the disordered iodine chains.

Introduction

During the past 15 years a series of partially oxidized one-dimensional molecular conductors has been prepared by chemical oxidation of porphyrinic metallomacrocycles (M(L)) with molecular iodine[1-9] or by electrochemical oxidation of the same porphyrins in the presence of a suitable electrolyte.[10-15] A single structural motif has been retained throughout this series of materials, that of metal-over-metal stacks of partially oxidized M(L) units surrounded by chains of anions. The arrangements of macrocycles in the stack can be described by an ABAB arrangement, with a rotation angle ϕ between adjacent A and B macrocycles in the unit cell. The highest conductivity in these systems occurs when ϕ is 45°, the angle that provides the greatest overlap of the a_{1u} HOMO π orbitals of the porphyrinic macrocycle.[3,16]

Although a few one-dimensional molecular conductors containing lower symmetry macrocycles are known,[17-20] the correlation between the π-orbital overlap and conductivity has not been examined for such systems. The molecular conductors M(dbtaa)I_2 (M = Ni, Pd)[21] have the same metal-over-metal structural motif with $\phi \approx 55°$.[17] These compounds are metallic and have room-temperature conductivities of 10–100 Ω^{-1} cm^{-1}.[17] In contrast, Ni(dtdbtaa)$I_{2.58}$ has a structure consisting of segregated stacks of macrocycles ($\phi = 0°$) that are slipped relative to one another so that there is no metal-over-metal arrangement.[19] This slip-stack motif is common for unoxidized aromatic macrocycles,[19,22] but it is unusual for one-dimensional molecular conductors. Despite the absence of a metal-over-metal arrangement, Ni(dtdbtaa)$I_{2.58}$ is metallic down to 180 K and has a room-temperature conductivity of 100 Ω^{-1} cm^{-1}. A one-dimensional molecular conductor based on a hexaazamacrocycle system derived from 1,10 phenanthroline has also been reported,[23] but details are lacking.

Here we report the new one-dimensional molecular conductor Ni(tprpc)$I_{1.67}$. This material is based on Ni(tprpc), the nickel(II) complex of the low-symmetry porphyrin analogue 2,7,12,17-tetrapropylporphycene.[22,24,25] The structure, charge-transport, and magnetic properties of Ni(tprpc)$I_{1.67}$ are reported.

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(21) Abbreviations used: dpg, 1,2-bis(diphenylglyoximato); bqd, 1,2-bis-(benzoquinone dioximato); pc, phthalocyaninato; omtbp, 1,4,5,8,9,12,13,16-octamethyltetrabenzoporphyrinato; tmp, 5,10,15,20-tetramethylporphyrinato; tprpc, 2,7,12,17-tetrapropylporphycenato; dbtaa, dibenzotetraazaannulene; dtdbtaa, ditolyldibenzotetraazaannulene.

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Table 1. Crystal Data

chem formula	$C_{32}H_{36}I_{1.67}N_4Ni$	space group	C_{2h}^6-$C2/c$
fw	746.96	Z	4
a, Å	22.548(5)	μ(Mo Kα), cm^{-1}	24.94
b, Å	4.982(1)	ρ_{calc}, g/cm^3	1.725
c, Å	27.156(5)	T, K	108(2)
β, deg	109.51(3)	$R(F_o)^a$ $(F_o^2 > 2\sigma(F_o^2))$	0.099
V, Å^3	2875.4(10)	$R_w(F_o^2)^b$ (all data)	0.209

^{a} $R(F_o) = \sum||F_o|-|F_c||/\sum|F_o|$. ^{b} $R_w(F_o^2) = \{\sum[w(F_o^2-F_c^2)^2]/\sum wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$; $w^{-1} = \sigma^2(F_o^2)$, $F_o^2 < 0$.

Table 2. Positional Parameters and U_{eq} Values (Å^2) for $Ni(tprpc)I_{1.67}$

atom	x	y	z	U_{eq}^a
I(1)	0	−0.5784(20)	$^1/_4$	0.043(2)
I(2)	0	−0.0391(25)	$^1/_4$	0.057(2)
I(3)	0	0.5744(23)	$^1/_4$	0.069(3)
I(4)	0	1.1758(25)	$^1/_4$	0.059(2)
I(5)	0	1.7259(24)	$^1/_4$	0.064(2)
Ni	$^1/_4$	$^1/_4$	$^1/_2$	0.0290(7)
N(1)	0.1635(3)	0.1567(21)	0.4686(3)	0.024(3)
N(2)	0.2342(3)	0.5081(20)	0.4468(3)	0.023(2)
C(1)	0.1188(5)	−0.0061(30)	0.4732(3)	0.035(4)
C(2)	0.0600(4)	0.0463(29)	0.4315(4)	0.031(4)
C(3)	0.0709(4)	0.2475(28)	0.4028(3)	0.020(2)
C(4)	0.1355(4)	0.3276(29)	0.4264(3)	0.032(4)
C(5)	0.1736(4)	0.5111(26)	0.4138(3)	0.024(3)
C(6)	0.1633(4)	0.7115(35)	0.3736(3)	0.042(4)
C(7)	0.2194(4)	0.8307(25)	0.3809(3)	0.024(3)
C(8)	0.2635(4)	0.7094(31)	0.4275(3)	0.028(3)
C(9)	0.3261(4)	0.7900(29)	0.4480(3)	0.027(3)
C(10)	0.3758(4)	0.7107(28)	0.4900(3)	0.024(3)
C(11)	−0.0015(4)	−0.1019(26)	0.4217(4)	0.030(3)
C(12)	−0.0551(4)	0.0117(29)	0.3774(4)	0.042(4)
C(13)	−0.1147(4)	−0.1471(26)	0.3660(4)	0.036(4)
C(14)	0.2336(4)	1.0316(28)	0.3471(4)	0.029(3)
C(15)	0.1781(5)	1.1077(26)	0.2992(4)	0.031(3)
C(16)	0.1940(5)	1.3240(29)	0.2664(4)	0.045(5)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j(U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j)$.

Experimental Section

Synthesis of Ni(tprpc). The compound Ni(tprpc) was synthesized by the literature method.[22]

Synthesis of $Ni(tprpc)I_{1.67}$. Unoxidized Ni(tprpc) (1–3 mg) was dissolved in dichloromethane or chloroform (3–4 mL) in the bottom portions of several diffusion tubes. These solutions were layered with saturated solutions of iodine in methanol, benzene, or hexane and were allowed to stand at 5 °C for up to 3 weeks. Golden rectangular needles of $Ni(tprpc)I_{1.67}$ were collected by filtration and washed lightly with methanol. Chemical analysis was performed by the Analytische Laboratorien, Gummersbach, Germany. Anal. Found: C, 41.83; H, 4.02; N, 5.92; I, 34.40. The C:H:N ratio of 32.0:36.6:3.9 derived from these data is in good agreement the expected ratio of 32:36:4. The iodine content is high, but it is difficult to obtain an accurate analysis for iodine because the material is contaminated with solid I_2 and loses it on standing at room temperature. The minimal amount of sample available for analysis precluded determination of the Ni content.

X-ray Diffraction Study of $Ni(tprpc)I_{1.67}$. Preliminary Weissenberg photography at room temperature established the crystal system and initial cell constants. These cell constants were refined by a least-squares analysis of the setting angles of 20 reflections that had been centered on a Picker diffractometer at 108 K. Intensity data were collected at 108 K with the ω scan technique and processed by methods standard to this laboratory.[26] No systematic changes were seen in the six standard reflections that were measured every 100 reflections. Systematic extinctions were consistent with the space groups C_{2h}^6-$C2/c$ and C_s^4-Cc. A total of 3240 reflections were measured; of the 2923 unique reflections, 1240 had $F_o^2 > 2\sigma(F_o^2)$. An absorption correction was applied.[27] Selected experimental details and crystal data may be found in Table 1, while additional details are available in Table SI.[28]

The centrosymmetric space group $C2/c$ was chosen on the basis of intensity statistics. The positions of the Ni, C, and N atoms were determined by direct methods.[29] This structure solution also contained positions along the 2-fold axis $(0, y, {}^1/_4)$ attributable to the I atoms. The electron density along this 2-fold axis consists of three broad peaks, of which two overlap and the third has two broad shoulders. The spectroscopic data (vide infra) are consistent with the iodine-containing species being I_5^-. With average I–I bond lengths and suitable intermolecular contacts, the length of an I_5^- ion corresponds closely to $3|b|$, and the distribution of electron density can be modeled by a single I_5^- ion occupying three unit cells along $0, y, {}^1/_4$. The individual I atoms in this model therefore have occupancy factors fixed at 0.167. Thus, the I:Ni ratio of 1.67:1 is fixed, and it agrees well with ratios determined by least-squares refinements of earlier, less physically interpretable models. The resultant $+{}^1/_3$ charge predicted for the macrocycle is the same as that observed in several similar macrocyclic conductors.[2,3,30] This model is also consistent with the diffuse scattering observed at room temperature: An oscillation photograph about b shows diffuse lines corresponding to $k' = \pm 1$ in an iodine lattice having $b^{*\prime} = {}^5/_3 b^*$, and hence to an average I–I distance of 3.14 Å along the iodine chains at room temperature. During the least-squares refinement[31] on F_o^2 the average intramolecular I–I distance was weakly restrained to be equal to 2.85 Å, and the thermal displacement parameters of the I atoms were restrained to be approximately isotropic. If no restraints were applied, convergence was still achieved with marginal improvement of agreement indices but with thermal ellipsoids that were unduly elongated in the y direction and with I–I distances that were unreasonable. Even with the restraints, the thermal displacement parameters of the I atoms are somewhat elongated along y, probably because of some disorder. The final refinement included anisotropic thermal displacement parameters for all non-hydrogen atoms and a riding model for hydrogen atoms (193 variables, 34 restraints, 2923 observations). It converged to a value of $R_w(F_o^2)$ of 0.209 (for all 2923 observations) and to a value of $R(F_o)$ of 0.099 (for 1240 reflections having $F_o^2 > 2\sigma(F_o^2)$). The mediocre agreement achieved undoubtedly reflects our inability to model the iodine scattering in a completely satisfactory manner. Final positional and equivalent isotropic thermal displacement parameters are listed in Table 2. Anisotropic thermal displacement parameters for the non-hydrogen atoms are given in Table SII,[28] and final positional and isotropic thermal displacement parameters for hydrogen atoms are reported in Table SIII.[28]

Raman Spectroscopy. Raman spectra were obtained as described previously.[32]

Single-Crystal Electrical Conductivity Measurements. The single-crystal electrical conductivity of $Ni(tprpc)I_{1.67}$ was measured along the needle (b) axis with the use of a four-probe ac (27 Hz) phase-locked technique, as described elsewhere.[33]

Magnetic Measurements. Room-temperature and variable-temperature EPR spectra were obtained from the bulk samples on a modified Varian E-4 X-band (9.0 GHz) spectrometer, with DPPH as a standard.[1] These data cannot be interpreted quantitatively owing to the presence of iodine-containing impurities.

Extended Hückel Calculations. These calculations were performed with the program CACAO[34] on (2,7,12,17-tetramethylporphycenato)nickel(II). The parameters were set at their default values, and the input coordinates were taken from the crystallographic coordinates for $Ni(tprpc)I_{1.67}$.

Results and Discussion

Structure of $Ni(tprpc)I_{1.67}$. The Ni(tprpc) macrocycle has a crystallographically imposed center of inversion. The macrocycles are arranged in a slip-stack motif similar to those in the structures of $Ni(dtdbtaa)I_{2.58}$ and the unoxidized macrocycles Ni(tprpc) and Ni(dtdbtaa).[19,22] In $Ni(tprpc)I_{1.67}$ the slip stacks have ϕ =

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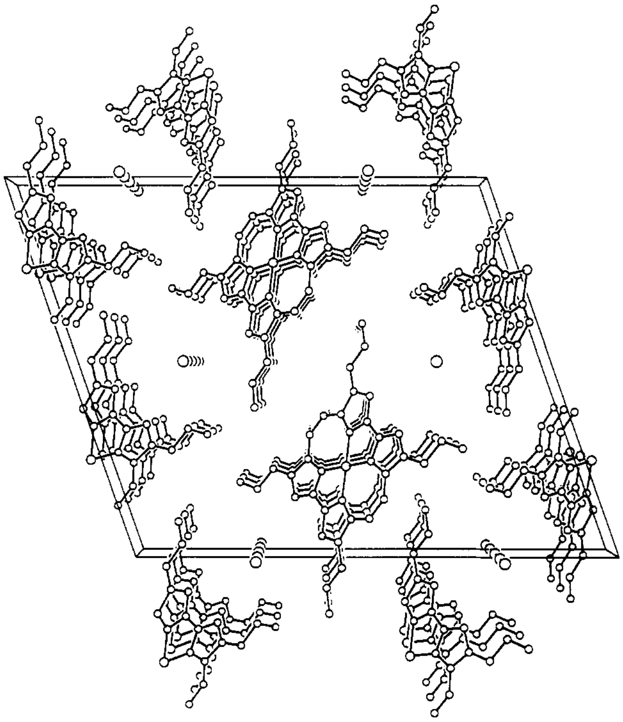

Figure 1. A view of three unit cells of Ni(tprpc)I$_{1.67}$ along *b*.

0°, with the propyl arms enclosing channels that contain the iodine chains (Figure 1). All four propyl arms of each macrocycle are coplanar with the aromatic core. The nickel atoms form lines parallel to *y*, but the slip stacking is manifested in angles less than 90° between *y* and the macrocyclic planes. For half of the stacks this angle is +42(1)°, while for the other half the angle is −42(1)°, so that the angle between Ni(tprpc) units in adjacent slip stacks is 84(1)°. The interplanar distance between Ni(tprpc) macrocycles is 3.306(10) Å, whereas the Ni–Ni distance is the *b* axis repeat distance, 4.982(1) Å; each macrocycle is slipped with respect to its neighbor by 3.73(2) Å. This Ni–Ni distance is longer than those in Ni(dtdbtaa)I$_{2.58}$ (4.075 Å)[19] and most other one-dimensional molecular conductors. The interplanar distance is within the range of those in Ni(tmp)I (3.466(3) Å),[3] [Ni(tmp)]$_2$[PF$_6$] (3.497(1) Å),[10] Ni(pc)I (3.244(2) Å),[2] and [Ni(dpg)]$_2$I (3.063(1) Å).[35,36] The shortest intermolecular contacts between Ni(tprpc) units involve the H atoms of the propyl groups, specifically H(3)···H(11B′) (2.48 Å), H(16C)···H(15B′) (2.53 Å), and H(14A)···N(2′) (2.78 Å).[37] The closest non-hydrogen intermolecular contact is C(4)···C(10′), 3.301(8) Å.

The bulk of the propyl groups and the modest steric requirements of the linear iodine chains provide an explanation for the slip-stack packing adopted by the macrocycles in this structure. If the macrocycles were arranged metal-over-metal perpendicular to the stacking direction, then the channels formed would be too large to be filled by the linear iodine chains. With the slip-stack packing, however, the channels close around the iodine chains.

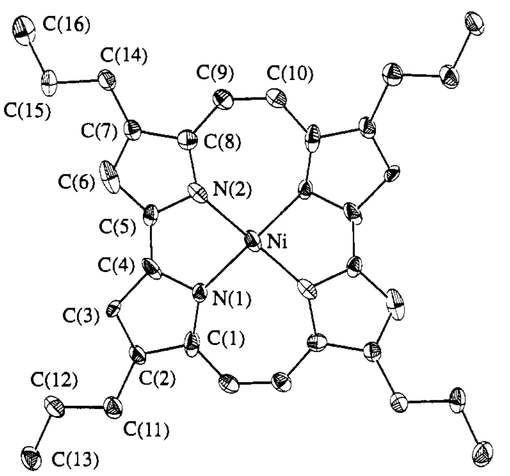

Figure 2. Structure of Ni(tprpc)I$_{1.67}$, as viewed perpendicular to the molecular plane, with 50% probability ellipsoids shown. Hydrogen atoms are omitted for clarity.

Table 3. Bond Distances (Å) and Angles (deg) for Ni(tprpc)I$_{1.67}$

I(1)–I(2)	2.687(10)	C(3)–C(4)	1.438(12)
I(2)–I(3)	3.056(8)	C(4)–C(5)	1.37(2)
I(3)–I(4)	2.996(9)	C(5)–C(6)	1.44(2)
I(4)–I(5)	2.740(10)	C(6)–C(7)	1.350(15)
Ni–N(2)	1.877(9)	C(7)–C(8)	1.454(13)
Ni–N(1)	1.908(8)	C(7)–C(14)	1.465(14)
N(1)–C(1)	1.331(14)	C(8)–C(9)	1.392(13)
N(1)–C(4)	1.398(13)	C(9)–C(10)	1.363(12)
N(2)–C(5)	1.360(11)	C(11)–C(12)	1.500(13)
N(2)–C(8)	1.396(15)	C(12)–C(13)	1.500(14)
C(1)–C(2)	1.452(12)	C(14)–C(15)	1.521(12)
C(2)–C(3)	1.34(2)	C(15)–C(16)	1.51(2)
C(2)–C(11)	1.514(14)		
N(2)–Ni–N(2′)	180	C(5)–C(4)–C(3)	134.4(10)
N(2)–Ni–N(1)	85.4(3)	N(1)–C(4)–C(3)	108.0(10)
N(2)–Ni–N(1′)	94.6(4)	N(2)–C(5)–C(4)	113.8(9)
N(1)–Ni–N(1′)	180	N(2)–C(5)–C(6)	112.3(10)
C(1)–N(1)–C(4)	107.4(8)	C(4)–C(5)–C(6)	133.9(9)
C(1)–N(1)–Ni	143.0(7)	C(7)–C(6)–C(5)	106.7(9)
C(4)–N(1)–Ni	109.5(7)	C(6)–C(7)–C(8)	106.3(10)
C(5)–N(2)–C(8)	104.0(8)	C(6)–C(7)–C(14)	126.8(10)
C(5)–N(2)–Ni	113.9(7)	C(8)–C(7)–C(14)	126.8(9)
C(8)–N(2)–Ni	142.1(6)	C(9)–C(8)–N(2)	126.9(10)
N(1)–C(1)–C(10)	128.4(9)	C(9)–C(8)–C(7)	122.4(12)
N(1)–C(1)–C(2)	109.9(10)	N(2)–C(8)–C(7)	110.7(8)
C(10)–C(1)–C(2)	121.7(11)	C(10)–C(9)–C(8)	133.8(13)
C(3)–C(2)–C(1)	106.9(10)	C(9)–C(10)–C(1)	131.1(11)
C(3)–C(2)–C(11)	126.7(9)	C(12)–C(11)–C(2)	113.7(10)
C(1)–C(2)–C(11)	126.5(11)	C(13)–C(12)–C(11)	113.1(11)
C(2)–C(3)–C(4)	107.7(9)	C(7)–C(14)–C(15)	114.6(9)
C(5)–C(4)–N(1)	117.4(8)	C(16)–C(15)–C(14)	113.1(9)

Bond distances and angles of the Ni(tprpc) macrocycle of Ni(tprpc)I$_{1.67}$ are listed in Table 3; they are comparable to those found in the unoxidized material.[22] The Ni(tprpc) macrocycle in Ni(tprpc)I$_{1.67}$ is highly planar, with the mean deviation from the plane for all non-hydrogen atoms (including propyl carbon atoms) being 0.057(2) Å (Figure 2). In contrast, only two propyl arms are coplanar with the macrocyclic core in the structure of unoxidized Ni(tprpc). While the I–I bond lengths correspond well with those expected for I$_5^-$,[38,39] care must be taken in their interpretation because the iodine parameters were not freely refined.

Raman Measurements. The Raman spectrum of a polycrystalline sample of Ni(tprpc)I$_{1.67}$ is shown in Figure 3. The spectrum is comparable to those of several I$_5^-$ species, with strong bands at 109 and 168 cm^{-1} and medium bands at 214 and 425 cm^{-1}.[38–41] The assignment of the iodine species as I$_5^-$ implies a +$^1/_3$ oxidation state for the nickel macrocycle, a common one among one-

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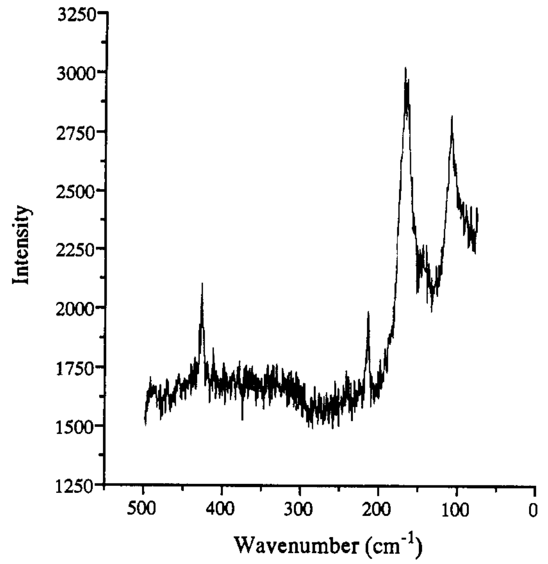

Figure 3. Raman spectrum (5145-Å excitation) of Ni(tprpc)$I_{1.67}$.

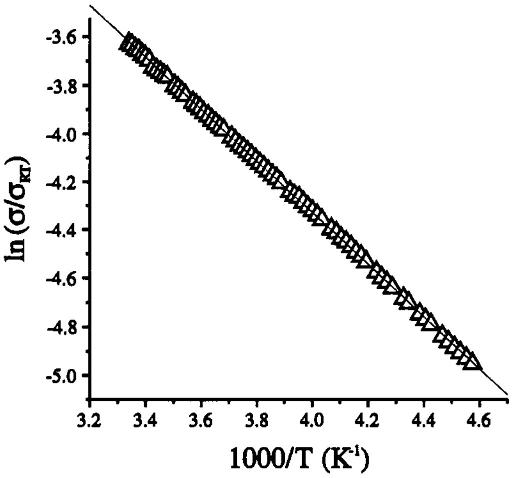

Figure 4. Temperature dependence of the conductivity of Ni(tprpc)$I_{1.67}$ relative to the room-temperature value of $\sigma_{RT} \approx 2.5 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$. The solid line is derived from the least-squares fit to the expression $\sigma = \sigma_0 \exp(-\Delta E/k_BT)$ ($\sigma_0 \approx 1$, $\Delta E = 0.15(2)$ eV).

dimensional molecular conductors.[2,3,30] The presence of free I_2 as an impurity in the sample cannot be established from the Raman spectrum owing to overlap of the I_2 bands at 215 and 425 cm^{-1} with those of I_5^-.[42]

EPR Measurements. The EPR spectrum of Ni(tprpc)$I_{1.67}$ powder shows a single signal with g = 2.0019(2) at room temperature, corresponding to the free-electron g value (2.0023). As the impurity in the sample is probably I_2 with no magnetic spin, we can still assign the site of oxidation on the Ni(tprpc) ligand. The line width at room temperature (16.3 G) is similar to that of [Pd(tmp)]$_2$[ReO$_4$] (13.5(2) G), both being in the characteristic range for π radicals. This assignment is supported by the extended Hückel calculation. For Ni(tprpc)$I_{1.67}$ the g value remains constant with decreasing temperature, but the line width decreases to 6.6 G at 230 K and remains approximately constant to 129 K, the lowest temperature of measurement. Similar changes in line width are seen in Ni(pc)I,[2,43,44] Ni(tmp)I,[3] [Ni(tmp)]$_2$[ReO$_4$],[11] and Ni(omtbp)$I_{1.08}$.[45] In Ni(pc)I and Ni(tmp)I such decreasing line widths are explained in terms of enhanced motional narrowing from a reduction in carrier mobility with decreasing temperature. However, enhanced motional narrowing cannot account for the decreasing line widths in the semiconducting systems Ni(tprpc)$I_{1.67}$, [Pd(tmp)]$_2$[ReO$_4$], [Ni(tmp)]$_2$[ReO$_4$], and Ni(ombtbp)$I_{1.08}$, where the conductivities decrease with decreasing temperature. An alternative explanation, proposed for Ni(ombtbp)$I_{1.08}$ and possibly pertinent here, ascribes this behavior to the temperature dependence of the correlated hopping of charge carriers.

Single-Crystal Electrical Conductivity. The conductivity of Ni(tprpc)$I_{1.67}$ measured along the needle (b) axis is $2.5 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at room temperature. The conductivity decreases with decreasing temperature in an activated fashion and may be fit to the expression $\sigma = \sigma_0 \exp(-\Delta E/k_BT)$ where ΔE is the activation energy and k_B is Boltzmann's constant. A least-squares fit to the data (Figure 4) yields an activation energy of 0.15(2) eV. The room-temperature conductivity of Ni(tprpc)$I_{1.67}$ is smaller than those of the semiconductors [M(tmp)]$_2$[ReO$_4$] (10–100 Ω^{-1} cm^{-1})[11-13] and [Ni(dtdbtaa)][I]$_{2.58}$ (100 Ω^{-1} cm^{-1}),[19] but greater than those of the semiconductors [M(bqd)]$_2$I$_{0.5}$ (8×10^{-3} to $1 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$)[46] and [M(dpg)]$_2$I (0.1 to $1 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$).[36] Activation energies in these systems are comparable.

The low conductivity of Ni(tprpc)$I_{1.67}$ can be ascribed to poor overlap of the ligand π orbitals resulting from the slip-stack packing. As an example, in Ni(pc)I, which is highly conducting, there are eight short interstack contacts between the pyrrole α-carbon atoms on adjacent molecules, and these carbon atoms make appreciable contributions to the partially occupied π MO of [Ni(pc)]$^+$ that forms the conduction band of the partially oxidized crystals. In contrast, in the present compound there are only two short contacts between atoms that contribute to the HOMO—C(4)···C(10′) = 3.30 Å and C(1a)···C(5a′) = 3.34 Å—and one of these involves atom C(4) at a node in the HOMO. Thus, the intra-stack transfer matrix element must be anomalously low.

As the bulky propyl groups probably cause the slip-stack motif, attempts are underway to synthesize one-dimensional conductors from tetramethylporphycene.

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Supplementary Material Available: Tables of experimental crystallographic details, anisotropic thermal displacement parameters, and hydrogen atom parameters (4 pages). Ordering information is given on any current masthead page.

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