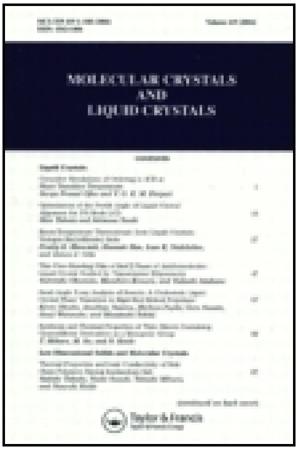

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Carrier Properties of Porphyrinic Molecular Metals

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CARRIER PROPERTIES OF PORPHYRINIC MOLECULAR METALS

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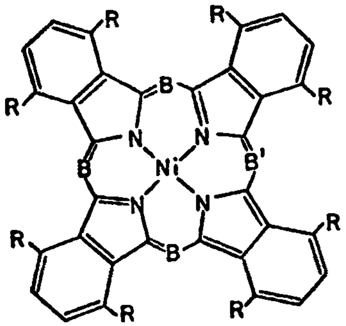
A series of quasi one-dimensional molecular metals based on metallomacrocycle building blocks is compared. The group of compounds Ni(L)I, where L = dianion of phthalocyanine (PC), tetrabenzporphyrin (TBP), or triazatetrabenzporphyrin (TATBP), are isoionic and isostructural but the nature of the charge carrier is quite different in each material. Oxidation in Ni(PC)I is exclusively from ligand π-orbitals so that conduction is associated with delocalized π-orbitals. Ni(TBP)I and Ni(TATBP)I display epr spectra that demonstrate that oxidation has occurred from both ligand π-orbitals and Ni d-orbitals so that these compounds display a novel, doubly mixed-valence state. The compounds Ni(PC)I, Ni(TMP)I, and Ni(OMTBP)I (TMP = tetramethylporphyrin, OMTBP = octamethyltetrabenzporphyrin) form an isoionic series where Coulomb correlations are of progressively greater importance.

INTRODUCTION

We have been studying highly conducting quasi one-dimensional molecular solids built from metallomacrocycles that may be viewed as variants on the porphine skeleton.[1-7] Like the "organic metals",[8,9] these molecular solids can attain high electrical conductivity, but the chemical flexibility of these metallomacrocycles provides a unique opportunity to vary the electronic properties of the molecular building block, and therefore the properties of the resulting solid.[10-13] In this paper we discuss some of our results. We first compare the properties of a suite of compounds, Ni(L)I, employing variants to the porphyrin skeleton:



R = H, B=B'=N; M(PC)

B=N B'=CH; M(TATBP)

B=B'=CH; M(TBP)

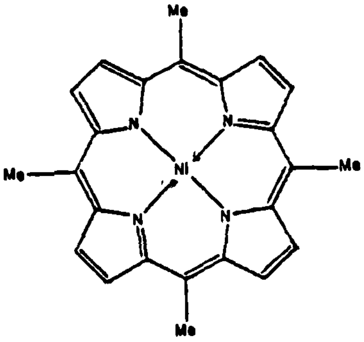
R = CH_3, B=B'=CH; M(OMTBP)

The tetrabenzporphyrin (TBP) skeleton can be viewed as having an expanded aromatic π-electron system obtained by fusing benzene rings onto the β-carbon atoms of the porphyrin pyrrole rings. Phthalocyanine (PC) may be imagined to arise from four methine → aza bridge substitutions in TBP. The "intermediate" complex, triazatetrabenzporphyrin (TATBP), conceptually can be obtained from TBP by three methine → aza bridge substitutions. The electronic properties of the subunits vary substantially without corresponding changes in steric structural features, and the conducting Ni(L)I are not only isostructural, but also are partially oxidized and isoionic.

Probably the most unusual result of this comparison concerns the nature of the charge carriers in these materials. The carriers in conducting molecular crystals have been found previously to belong to one of two limiting classes. Either they are confined to the d orbitals of a conducting metal spine as in the tetracyanoplatinate salts, or they are associated with delocalized π molecular orbitals as in the organic conductors.[8,11] We have now found the first well characterized partially oxidized complexes in which the charge carriers exhibit both metal and ligand properties. It appears that the electron hole created by iodine oxidation of Ni(TBP) and Ni(TATBP) can jump between the metal and the macrocycle, as well as between one

Ni(TBP) unit and its neighbors. In short, these complexes display a novel, doubly mixed-valence state.

We also discuss the structural, magnetic, and charge transport properties of single crystals of the small-ring porphyrin system Ni(TMP)I, a highly conducting compound obtained by partial oxidation of tetramethylporphyrinatonickel(II), Ni(TMP), with iodine.



Small-ring porphyrin systems are of interest because their conjugated framework is much less extensive than that of their large-ring counterparts. In particular, we find that the variation of the ring size has important consequences for the relative importance of electron correlation effects within the conducting metallomacrocyle stacks.

Ni(L), L=PC, TBP, TATBP

Iodine oxidation of Ni(PC),[1-3] Ni(TBP),[4] and Ni(TATBP)[5,6] in each case leads to isolation of crystals with composition Ni(L)I. Full X-ray diffraction, resonance Raman, and ^{129}I Mossbauer studies show that the first two iodinated materials are isostructural and isoionic, consisting of columnar stacks of planar metallomacrocycles with parallel (disordered) chains of triiodide counterions (Figure 1).

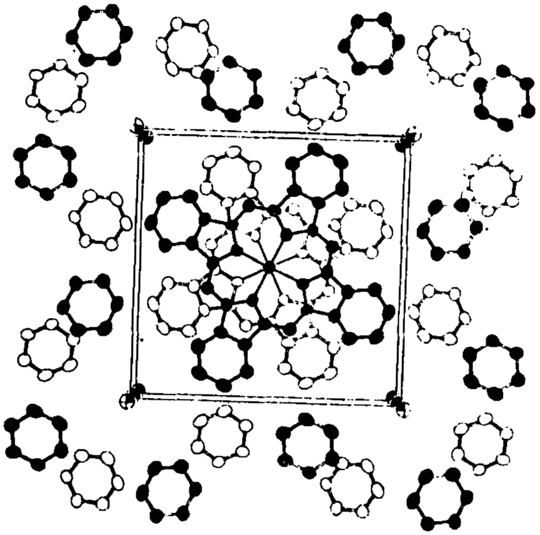


Fig. 1. Structure of Ni(PC)I and Ni(TBP)I as viewed down the c (stacking) axis.

Thus, the materials are in a non-integral oxidation state that may be written formally as $(Ni(L))^{+0.33}(I_3^-)_{0.33}$. Furthermore, X-ray photographs and resonance Raman spectra of the Ni(TATBP)I[14] system are identical to those of Ni(PC)I and Ni(TBP)I, so all three of these systems appear to be structurally equivalent. The metallomacrocycle in each of these compounds is on a site of 4/m symmetry and consequently is crystallographically constrained to be planar. Thus, there is no impediment to strong intrastack interactions, and short metal-metal spacings along a Ni(L) column reflect this: Ni(PC)I, 3.244(2) Å at 298°K,[1] Ni(TBP)I, 3.26(2) at 298°K and 3.217(5) Å at 116°K.[4] However, the electronic properties of the three Ni(L) parent molecules differ significantly because of the different electronegativities of the (-N=) and (-CH=) bridges.[14] Since the Ni(L)I crystals exhibit no concomitant changes in ionicity or structure, they offer an opportunity to examine the dependence of solid state properties on purely electronic characteristics of the subunit in the absence of competing effects.

Each of the three materials shows a reduced and nearly temperature-independent paramagnetic susceptibility, χ^S, corresponding to $\sim$ 0.1 spins/macrocycle at room temperature. Relating χ^S to the Pauli susceptibility of a one-dimensional tight-binding band[5,15] affords us an estimate of the intermolecular interactions within a stack, and in each case we obtain $|t| \sim 0.1$ eV.

Room-temperature conductivities and, of more significance, mean-free-paths for carrier motion along the stack are comparable with values reported for other one-dimensional "metals", including the organic charge-transfer salts.[5,16] Both Ni(PC)I and Ni(TBP)I show metal-like increase in conductivity upon cooling from room temperature but the resistivity of the former accurately varies with $T^{1.9}$, while that of the latter changes more gradually. The major difference in the temperature dependence of the conductivity for these compounds occurs at lower temperatures. The conductivity for Ni(TBP)I reaches a broad maximum before falling off rapidly. In contrast, the conductivity of Ni(PC)I increases with decreasing temperature until it reaches a maximum value of $\sim 1500\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at ca. 55°K, but undergoes a discontinuous transition to a semiconducting state with further cooling. The characteristics of Ni(TATBP)I follow the temperature response of Ni(TBP)I, but are not simply intermediate between those of Ni(PC)I and NI(TBP)I, although the room temperature conductivity is comparable.

The carrier spin g-values and linewidths (Γ) for Ni(TBP)I and Ni(TATBP)I are anomalous; both quantities are unusually large at room temperature (for Ni(TBP)I, $g_{av} = 2.03$, $\Gamma = 105$ G) and increase strongly as the temperature is lowered (Figure 2). Moreover, the epr linewidths show an unprecedented increase with increasing spectrometer frequency.[4,6] This may be contrasted with the frequency independent linewidths of Ni(PC)I, Ni(OMTBP)I, and, for example, TTF-TCNQ. The frequency dependence of the linewidth requires that the carrier interchange between ligand and metal occurs with a frequency, ω_i, that is only marginally larger than the frequency difference between the resonance frequency for a pure metal d spin and a pure ligand π radical (i.e., at X-band, $\omega_i > \beta\ (g_{Ni}-g_L)H_o/h \sim 10^9$-$10^{10}$ sec^{-1}). In order to describe the unusual frequency and temperature dependence of the epr properties of the doubly

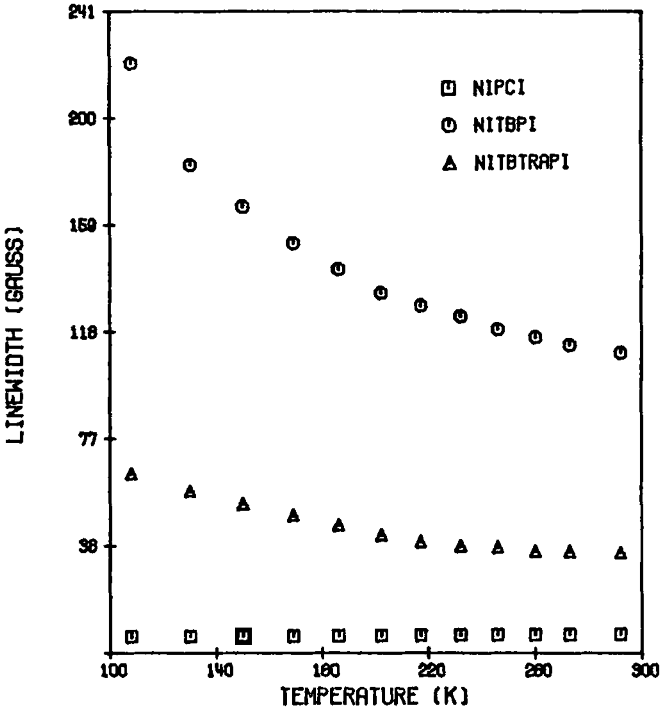


Fig. 2. Temperature dependence of the epr linewidth for Ni(PC)I, Ni(TBP)I, and Ni(TATBP)I.

mixed-valent materials Ni(TATBP) and Ni(TBP)I, a model based on the modified Bloch equations for two-site exchange has been employed.[17,18] The physical model for these materials is that the spin-bearing hole can hop between one of two sites: the oxidation can be metal-centered to form a Ni^{III} species with g value g_d and linewidth Γ_d or the oxidation can be ligand-centered to form a π-cation radical with g value g_π and linewidth Γ_π. The equations for the coupled magnetization equations then depend on the lifetime on each site, τ_π and τ_d. The observed frequency dependence of the linewidth implies that exchange is neither in the fast nor the slow limits, and thus the magnetization equations must be solved exactly.

All parameters may be estimated from reference epr spectra except for three: Γ_d, τ_π, and τ_d. The principle of detailed balance requires that the ratio τ_π/τ_d be equal to the ratio of the magnetic susceptibilies of each site, χ_π/χ_d, thus introducing a further constraint if the single site susceptibilities can be deduced. The room temperature frequency dependence of the linewidth can be used to set the three free parameters and we find the lifetimes to be slightly different for the two systems; for Ni(TATBP)I $\tau_\pi = 3\times10^{-9}$ sec and $\tau_d = 3\times10^{-10}$ sec while for Ni(TBP)I $\tau_\pi = 1\times10^{-9}$ sec and $\tau_d = 4\times10^{-10}$ sec. In terms of $g=2$, $S=1/2$ spins the total spin susceptibility for Ni(TBP)I is 0.10 spins per macrocycle implying the equivalent of 0.03 Ni^{III} spins per macrocycle and 0.07 π-cation radical spins per macrocycle at room temperature. For Ni(TATBP)I these values are 0.01 Ni^{III} spins per macrocycle and 0.12 π-cation radical spins per macrocycle.

The temperature dependence of the linewidth can be reproduced by allowing τ_d/τ_π and Γ_d to vary with temperature, leaving the other intrinsic site parameters constant. In both cases the temperature dependence of the ratio $\chi_d/\chi_\pi = \tau_d/\tau_\pi$ has very nearly a T^{-1} behavior. Since χ_π should be roughly temperature independent, as seen with Ni(PC)I and Ni(TMP)I, this indicates that the magnetization associated with the nickel spins has the nearly Curie-like behavior of spins that interact only weakly. This is not surprising because the density of Ni^{III} sites is low. The model is consistent with the temperature dependence of the g values as well. As the temperature is lowered χ_d/χ_π increases, thus increasing the weighting of g_d and the observed g-value.

Ni(TMP)I

Crystallographic studies of Ni(TMP)I show that the Ni(TMP) molecules are ruffled (S_4) and are stacked metal-over-metal such that their mean molecular planes are perpendicular to the crystallographic c axis. They alternate in an ABAB pattern along c, where molecule B is related by symmetry to molecule A but is rotated about its S_4 axis by 37°. Disordered chains of triiodide ions run parallel to the c axis, and thus this compound has the same ionicity as do the large ring compounds, with an average oxidation level of $[Ni(TMP)]^{+0.33}$. The Ni-Ni separation of 3.466(3) Å (c/2)[19] is about 0.2 Å longer than that found in Ni(PC)I,[1] and Ni(TBP)I.[4]

The room-temperature value of the electrical conductivity along the needle axis of single crystals of Ni(TMP)I ranges from 40 to 270 $\Omega^{-1}cm^{-1}$ with an average value of 110 $\Omega^{-1}cm^{-1}$. This value, which is comparable with values found for "organic metals" such as NMP-TCNQ (100-400 $\Omega^{-1}cm^{-1}$),[20] is in the same range as that of Ni(TBP)I (150-330 $\Omega^{-1}cm^{-1}$),[4] slightly lower than that of Ni(PC)I (260-750 $\Omega^{-1}cm^{-1}$),[1] and an order of magnitude larger than that of the polaronic conductor Ni(OMTBP)$I_{1.08}$ (4-16 $\Omega^{-1}cm^{-1}$).[7] As the temperature is lowered from 298°K, the conductivity shows a metal-like increase until it reaches a maxiumum value at a temperature $T_m \sim 115 \pm 10$°K where the conductivity is approximately twice the room-temperature value, and then falls rapidly. For heuristic purposes it is useful to calculate a carrier mean free path, $\lambda_{\parallel}$. At room temperature, $\lambda_{\parallel}$ for Ni(TMP)I ranges from 0.07 to 0.46 times the intermolecular spacing, d = c/2. A value of $\lambda_{\parallel}/d < 1$ is indicative of a diffusive, or hopping, conductor.

At 298°K, the spin susceptibility for a single crystal of Ni(TMP)I is high, corresponding to ~ 0.3 per macrocycle at 298°K, and it is essentially temperature independent down to a transition temperature of 28°K (Figure 3).

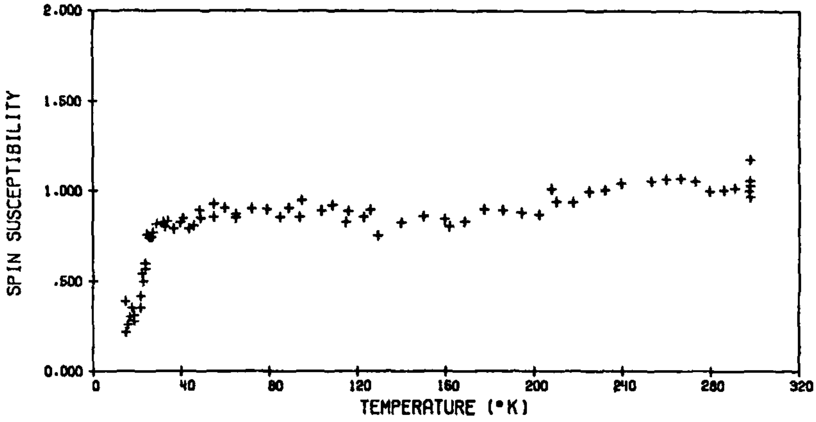


Fig. 3. Temperature dependence of the relative spin susceptibility of Ni(TMP)I.

At temperatures below the transition, the susceptibility decreases in an activated fashion $\chi \sim (T)^{-1} \exp(\Delta/kT)$ with an activation energy, $\Delta/k \sim 60^\circ K$. The organic conductor $(TMTTF)_2X$,[21] $X = ClO_4^-$, BF_4^- exhibits magnetic behavior that is very similar to that of Ni(TMP)I, with both a high room-temperature paramagnetism and temperature-independent susceptibility accompanied by a low-temperature transition to a singlet ground state. In the Ni(TBP)I[4] and Ni(PC)I[1] systems, where the measured paramagnetism is low ($\sim$ 0.1 spins per macrocycle compared with ionicity value of 0.33), the observed temperature-independent susceptibility was described as Pauli-like and for illustrative purposes was modeled in terms of a tight-binding band of noninteracting electrons. However, it clearly is not appropriate to describe the temperature-independent susceptibility of Ni(TMP)I ($30^\circ K < T < 298^\circ K$) in this fashion because at room temperature the effective spin concentration is as high as the ionicity, $\rho = 0.33$.

The failure of the theory most probably reflects its neglect of electron correlation effects. The Hubbard model[22] is the simplest model that includes the effects of the on-site Coulomb repulsion, U. With the inclusion of a small U, $U/4t \ll 1$, an enhanced Pauli paramagnetism is predicted. The properties of the $(TMTTF)_2X$ have been interpreted in this manner. When U becomes very large, $U/4t \gg 1$, the spins associated with the carrier behave as though they interact by an antiferromagnetic exchange interaction of magnitude $J \sim 4t^2/U$, and a high conductivity can nonetheless be associated with a large and weakly temperature-dependent susceptibility. Employing theoretical calculations for such a case we find that an effective exchange interaction of $J \sim 200\ cm^{-1}$ will reproduce the susceptibility data for Ni(TMP)I reasonably well. The analysis in terms of an antiferromagnetically coupled spin system suggests the possibility that the sharp decrease in the susceptiblity of Ni(TMP)I at 28°K may be caused by a spin-Peierls transition.

DISCUSSION

Probably the most unusual result that emerges from the comparison concerns the nature of the charge carriers. In the large-ring systems, analysis of the Ni(PC)I g-tensor showed that the metal retains its formal Ni^{II} oxidation state, playing a secondary role in the conduction process, and that the charge carriers are associated with delocalized π-orbitals on the macrocycle. However, the g-value and linewidth results indicate that Ni(TBP)I and Ni(TATBP)I are the first partially oxidized complexes in which the charge carriers exhibit both metal and ligand properties and thus these complexes display a novel, doubly mixed valence state. The electron hole created by iodine oxidation can carry charge by jumping between one Ni(L) unit and its intrastack neighbors, and also can jump between the metal and the macrocycle, the $[Ni(L)]^+$ cation itself thus exhibiting interconversion between the electronic tautomers, $[Ni^{II}(L)^+]$ and $[Ni^{III}(L)]$.[5]

The results with Ni(TMP)I show that changing the size of the conjugated molecular π-system also can substantially change the character of the charge carriers. The large-ring systems, such as Ni(PC)I appear to be usefully pictured by the simple construction of a tight-binding metal with delocalized states and wave-like conduction, as suggested by the result that $\lambda_\parallel/d > 1$. On the other hand, it seems clear that Coulomb correlations play a major role in determining the magnetic properties of Ni(TMP)I and that U/4t is greater for this compound than for Ni(PC)I or Ni(TBP)I. It is also interesting to compare Ni(TMP)I and Ni(OMTBP)$I_{1.08}$. The Curie-like susceptibility observed for this latter compound indicates that its unpaired spins are highly localized,[7] and requires that Ni(OMTBP)$I_{1.08}$ represent the limit of very weakly interacting building blocks where Coulomb interactions dominate: $4t/U \to 0$. In this case, which is often referred to as the "atomic limit", a large value of U/4t is obtained because poor intermolecular overlap and large intermolecular spacing ($d = 3.78$ Å) between nonplanar macrocycles make t vanishingly small. Thus comparisons among their physical properties show that Ni(PC)I, Ni(TMP)I and Ni(OMTBP)I form an isoionic series in which Coulomb correlations are of progressively greater importance, and that the relative importance of the correlation effects can be modified in an understandable fashion through controlled charges in the metallomacrocycle building blocks.

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