

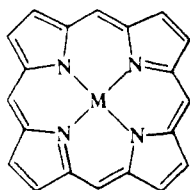
Porphyrinic Molecular Metals

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Studies of the electrical, magnetic, and structural properties of molecular crystals¹⁻¹⁰ provide a wealth of surprising results. Among these is the discovery of "molecular metals"¹⁻⁶ and molecular superconductors,⁷ terms that only a few years ago would have seemed self-contradictory. Most such studies have been concerned with the so-called "organic metals", typified by TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane). In this Account we summarize our research¹¹⁻²³ on highly conducting molecular crystals prepared from porphyrin and phthalocyanine complexes that may be viewed as derivatives of the metalloporphine skeleton:



Consider the porphyrinic complexes displayed in Figure 1. Each forms ordinary molecular crystals with electrical conductivity (σ) in the insulating range, ($\sigma < 10^{-10} \Omega^{-1} \text{cm}^{-1}$).²⁴ But if we react a given complex with iodine, we typically obtain a product that contains one iodine atom per metal atom and crystallizes as fine needles having a metallic luster. These crystals exhibit conductivity along the needle axis (σ_{\parallel}) some 12 orders of magnitude greater than the parent (Figure 2). Note also that σ_{\parallel} for these crystals increases as the temperature is lowered from ambient, as expected for a metal, reaches a maximum, and then in most *but not all* cases declines to a value typical for an insulator. What are the structures of these conducting molecular crystals? If iodine has been reduced, what has been oxidized—the metal, the porphyrin, or both—and by how much? What is the nature of the acceptor species, i.e., I^- , I_2 , I_3^- , ...? What controls σ_{\parallel} and can it be related to the properties of the macrocycle and the composition or structure of the material? Why does the temperature dependence of σ_{\parallel} vary with the porphyrin? Can we learn enough to contemplate tailor-making materials with desired physical properties? These and other basic questions evolve from a natural curiosity about such unusual compounds. But there are other interests as well. The features of conductive molecular crystals, for example metal-like conductivity, open up the possibility of their utilization as current control components (e.g.,

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Scheme I



sensors, inductors), polarizing optical materials, energy conversion elements, antistatic compounds, and perhaps superconductors.

The chemical flexibility of porphyrin-like metallo-macrocycles (M(L)) provides an opportunity to prepare a large class of new materials that are particularly valuable for the exploration of the relationships between molecular stereoelectronic characteristics and solid-state transport properties. These new materials exhibit not only high metallic conductivities but also unusual charge carrier properties. For example, the carriers in conducting molecular crystals have been found previously¹⁻⁷ 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,^{1-3,25} or they are associated with delocalized π molecular orbitals, as

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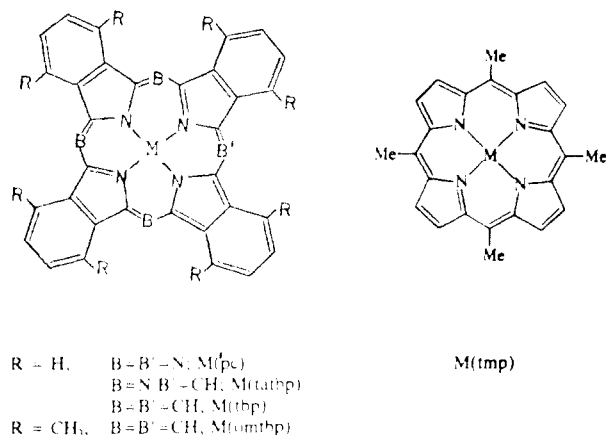


Figure 1. Porphyrinic complexes discussed in this Account.

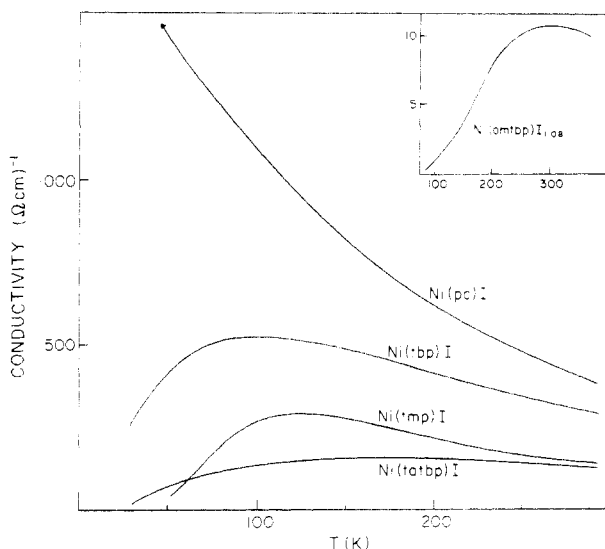


Figure 2. Temperature response of the conductivity along the stacking axis of several porphyrinic molecular conductors. References to original studies are given in text. Typical uncertainties are $\pm 10\%$ of the indicated values.

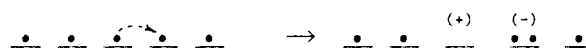
in the organic conductors. But among the oxidized metalloporphyrins we have found^{14,15} molecular conductors in which the charge carriers exhibit both metal and ligand properties and are able to jump between the metal and the macrocycle as well as between one molecule and its neighbors along a conducting metal-macrocycle stack.

In this Account we present the criteria that have evolved for creating conducting molecular crystals, describe the porphyrinic macrocycles that we employ, and discuss some of the relationships we have found between molecular stereoelectronic characteristics and solid-state properties.

Designing Molecular Metals

It appears that a molecular crystal based on a metal complex (or an organic molecule) can be highly conducting only if it meets two criteria. The first is that the metal-ligand molecules must be in crystallographically similar environments and be essentially planar, so that they are arrayed to achieve the intermolecular interactions necessary to generate a conductive pathway. Second, the metal-ligand complex must adopt a nonintegral oxidation state.^{26,27} This characteristic has

Scheme II



Scheme III



been referred to as "partial oxidation", "mixed valence", or "incomplete charge transfer", and although this nonintegral oxidation state has generally been effected with oxidizing agents, in principle it can equally well be achieved by partial reduction.

In order to appreciate the importance of a nonintegral oxidation state first consider the conduction process in a one-dimensional array of closed-shell molecules. In order to transport charge it is necessary first to separate positive and negative charges along a chain, and this requires a large activation energy (Scheme I). An equivalent picture is obtained from a simple band-theory argument that considers only the highest occupied molecular orbital of the $M(L)$ units; the interaction between sites that gives rise to mobility along the chain is written in terms of an electron transfer matrix element, t , and electron-electron repulsions are ignored. The theory, called the tight binding model,⁸ is formally identical with the Hückel theory for an infinite regular polyene, with the Hückel β renamed t .²⁸ In either case, for a chain of N sites the N localized single-site orbitals become a band of N delocalized states, called the valence band. The bandwidth is $4t$ (4β) and the energy spacing between levels is of order $4t/N$, vanishing for large N . From this model one predicts that a crystal of closed-shell molecules should be a semiconductor (or insulator), for it has a filled valence band and thus carrier generation requires excitation across a band-gap. In contrast, any open-shell system should be a metal if the disposition of molecules satisfies the first criterion above. In particular, a regular one-dimensional chain of atoms or molecules having an odd number of electrons per site should exhibit a partially filled band and metallic conductivity.

In fact, crystals of organic free radicals and of open-shell transition-metal complexes are for the most part no better conductors than are their closed-shell counterparts.²³ In order to transport charge in a crystal composed of parallel stacks of molecules with an integral number of electrons per site it is necessary to perturb the equilibrium electron distribution. For example, in an open-shell system states must be created with, say, two electrons on one site, none on another (Scheme II), and this disproportionation process is energetically unfavorable, just as is the process in Scheme I. But when the molecules in such a stack are in a nonintegral oxidation state, there is no need to change the population distribution among sites during charge transport and the carriers in such a structure are free to move by jumping from one site to another. For example, with closed-shell molecules that have been partially oxidized we might schematically envision charge transport by a limiting process in which preformed holes move between isoenergetic configurations

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Table I
Comparative Structural Features of Some Ni(L)I Complexes

compound ^a	crystallographic symmetry imposed on Ni(L) moiety	Ni-Ni, Å	Ni-N, Å	T, K	ref
Ni(pc)I	4/m → planar	3.244 (2)	1.887 (6)	298	11
Ni(tbp)I	4/m → planar	3.217 (5)	1.966 (9)	113	14
Ni(tmp)I	$\bar{4}$ → S ₄ ruffled	3.466 (3)	1.938 (3)	114	20
Ni(omtp)I _{1.08}	$\bar{4}$ → S ₄ ruffled	3.778 (3)	1.953 (5)	298	18

^a In all complexes listed I is in the form of I₃⁻.

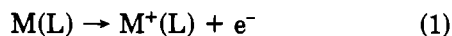
(Scheme III). All highly conductive organic compounds and transition-metal complexes known to date are of the partially oxidized class, and the evidence thus indicates that a nonintegral oxidation state is necessary if a molecular crystal is to conduct well.

Surprisingly, for a crystal to contain regular stacks of metallomacrocycles in a nonintegral oxidation state appears to be insufficient to ensure high conductivity. Various bis(glyoximate) complexes, including the diphenylglyoximate complex Ni(dpg)₂I,²⁹⁻³¹ possess the necessary requirements of structure and valency and yet are semiconductors with only modest room-temperature conductivities.

Porphyrinic Building Blocks

The utility of porphyrinic metallomacrocycles as building blocks for partially oxidized conducting molecular solids lies in the great scope they offer for variation of molecular architecture. In this Account we focus solely on nickel-porphyrin complexes and discuss the consequences of controlled variations in the porphyrinic macrocycle, both in the skeleton and in peripheral substituents. In addition to the porphyrins themselves, the three variants to the porphyrin skeleton that have been most extensively examined are tbp, pc, and tatbp (Figure 1). The 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. The pc ring may be imagined to arise from four methine → aza bridge substitutions in tbp. The intermediate complex, tatbp, can be viewed as a tbp that has undergone three methine → aza bridge substitutions.

The cation state generated by oxidation of a M(L) metallomacrocycle is of central importance in determining the characteristics of a partially oxidized molecular crystal. This state exhibits more variability than that of an oxidized organic compound, since both the central metal and the aromatic π system of the macrocycle can be redox active.^{32,33} For some divalent metal ions, such as Mn²⁺, Fe²⁺, Co²⁺, and Ag²⁺, the first oxidation of a neutral M(L) parent complex normally occurs at the metal atom, and the process can be written schematically



where the plus charge indicates the site of oxidation,

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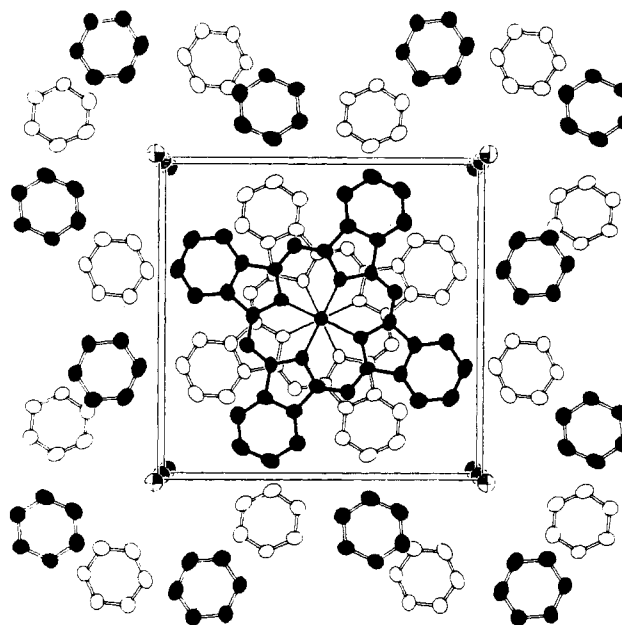
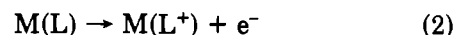


Figure 3. View down the c axis of the unit cell of Ni(pc)I (ref 11). The similar view for Ni(tbp)I (ref 14) is indistinguishable. Hydrogen atoms have been omitted for clarity.

not the formal valency. However, for metals without a readily accessible trivalent state, such as Mg²⁺ and Zn²⁺, as well as for systems such as (AlF)₂²⁺,^{34,35} the highest occupied orbital of the complex is a π molecular orbital of L, and the first oxidation is ligand centered. Such a process may be represented as



There are instances, however, where the metal- and ligand-oxidized states of an individual complex are roughly degenerate and are interconvertible. Thus, Ni(pc) can form either a ligand- or metal-oxidized species, depending on conditions.³² As we discuss below, conductive materials prepared from such molecules are of particular interest.

Structural Features of Iodine-Oxidized Metalloporphyrins

Molecular iodine has been an especially advantageous oxidant to achieve partial oxidation of these metallomacrocycles.^{11-22,29-31,34-38} The reasons are the stability of polyiodide anions (I₃⁻, I₅⁻) in nonpolar environments and the ready accommodation of such ions in channels in the various structures. Molecular bromine and other

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oxidants^{34,35} may be similarly useful, but have not been employed frequently. All of the iodine-oxidized systems discussed here exhibit a topology permitting the strong intermolecular interactions required by the first criterion discussed above. They crystallize with stacks of metallomacrocycles around which are parallel channels containing linear chains of iodine (Figure 3).^{11,14,18,20} Metallomacrocycles are stacked metal over metal, such that the mean molecular plane is perpendicular to the stacking (*c*) axis. They alternate in an ABAB pattern along *c*, where molecule B is related to molecule A by symmetry but is rotated about the stacking axis by $\sim 45^\circ$. Some comparative structural features are given in Table I. Note particularly that the Ni-Ni distances vary by more than 0.5 Å although the compounds crystallize with the same basic motif.

The nature of the macrocycle stacks and the general details of the crystal structures may be deduced from the usual X-ray diffraction techniques (Bragg scattering). However, the iodine chains are usually disordered, as evidenced by the occurrence of diffuse X-ray scattering, and both spectroscopic and diffraction methods are required to characterize them. Spectroscopic methods particularly sensitive to the molecular form of iodine include resonance Raman spectroscopy, which offers a simple means of characterizing polyiodide anions, and ¹²⁹I Mössbauer spectroscopy, which is used to quantitate the amount of I⁻ present, as well as to support the Raman assignment of polyiodide species.^{11,39,40} All the compounds discussed here are triiodide species. Mössbauer studies of Ni(pc)I confirm the triiodide identification and also rule out any significant proportion of I⁻; we assume the same to be true for the other compounds. Thus, since all the compounds listed in Table I have composition M(L)I, with the sole iodine-containing species being I₃⁻ ions, in each case the M(L) building blocks have been oxidized to the average extent of one-third electron per site, and the compounds may be written formally as (M(L))^{+0.33}(I₃⁻)_{1/3}. The average ionicity (charge) of the M(L) building blocks, $\rho = +0.33$, satisfies the nonintegral oxidation state criterion for a conductive molecular crystal.

If the lattices that describe the metal and iodine positions along *c* are commensurate, that is if their repeats are related to one another in a rational way, analysis of the diffuse X-ray scattering can reveal the spatial distribution of the iodine molecular species. The diffuse scattering from Ni(pc)I is consistent with a model that consists of ordered chains of symmetrical I₃⁻ units that are disordered (translated) with respect to their neighbors (Figure 4).¹¹ But if the lattices are incommensurate, which is often the case, analysis of the diffuse X-ray scattering is very difficult, and derivation of a unique model is impossible.^{15,18,20,41}

Charge Transport

Figure 2 displays single-crystal conductivity curves for several porphyrinic conductors: stacked metallomacrocycles in a nonintegral oxidation state indeed exhibit high room-temperature conductivities ($\sigma > 10^2$

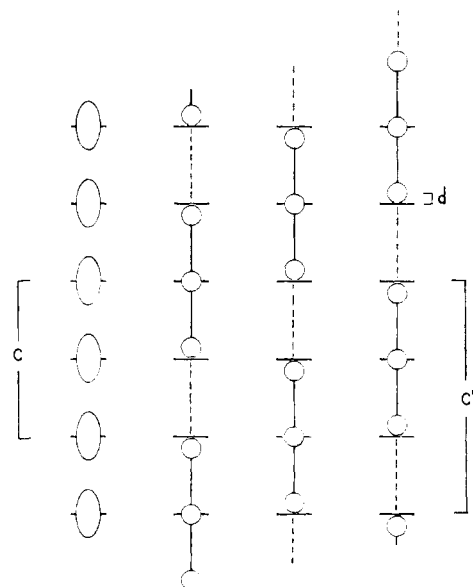


Figure 4. Model of the disorder of the iodine chains in Ni(pc)I. Average positions are shown on the left; the three distinct supercells, each containing three such sites, are shown with the same scale on the right (ref 11).

$\Omega^{-1} \text{ cm}^{-1}$) and metal-like behavior ($d\sigma/dT < 0$). Moreover, mean free paths for carrier motion along the stack, discussed presently, are comparable with values reported for other molecular metals, including the organic charge-transfer salts.

The compounds Ni(pc)I^{11-13,23} and Ni(tbp)I^{14,15} form a pair of particular interest. Full X-ray diffraction, resonance Raman, and ¹²⁹I Mössbauer studies show that they are isostructural and isoionic, but the methine \rightarrow aza bridge substitution makes a significant change in the electronic structure of the molecular building block. This change produces striking contrasts both in the charge transport properties of these metal-like conductors (Figure 2) and in their magnetic properties. Both Ni(pc)I and Ni(tbp)I show a metal-like increase in conductivity upon cooling from room temperature. However, the conductivity of Ni(tbp)I reaches a broad maximum and then falls off rapidly, in a fashion characteristic of quasi-one-dimensional systems. Such behavior may arise from the Peierls instability, the tendency of a regular conducting chain to undergo a periodic distortion that causes σ to vanish as $T \rightarrow 0 \text{ K}$.^{1-4,6,8} In contrast, the conductivity of Ni(pc)I increases with decreasing temperature¹¹⁻¹³ until it reaches a shallow maximum value of $\sim 5000 \Omega^{-1} \text{ cm}^{-1}$ at ca. 25 K and then decreases very slowly. As $T \rightarrow 0 \text{ K}$, σ does not vanish, but asymptotically approaches a high limiting value, $\sigma/\sigma(300 \text{ K}) \sim 1$.²³ Indeed, Ni(pc)I is the first molecular crystal that remains conductive at the lowest available temperatures (100 mK),²³ yet does not contain a chalcogen (S or Se) mediated pathway for strong interstack interactions. The conductivity curve of the "intermediate" compound Ni(tatbp)I is qualitatively like that of Ni(tbp)I, but does not fall between those of Ni(pc)I and Ni(tbp)I. The behavior of the small-ring metallomacrocyclic system Ni(tmp)I²⁰ is surprisingly similar to that of Ni(tbp)I. These similarities and differences raise fundamental issues about charge transport in molecular crystals.

An insight into the nature of the charge transport can be obtained by calculating the ratio of the carrier mean

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Table II
Comparison of Mean Free Paths for Some Organic
and Inorganic Molecular Conductors

compound ^a	room- temperature conductivity, $\Omega^{-1} \text{ cm}^{-1}$	mean free path, intermolecular spacings	ref
Ni(pc)I	300-1000	1.0-2.3	11
Ni(tbp)I	180-330	0.7-1.3	14
Ni(tatbp)I	110-200	0.4-0.8	16
Ni(omtpb)I _{1.08}	16	0.04	18
Ni(tmp)I	40-280	0.07-0.51	20
TTT ₂ I ₂	>1000	>2.0	b
HMTSF-TCNQ	1400-2200	1.6-2.5	c
TTF-TCNQ	500-1000	0.4-0.8	d
KCP	100	0.6	2

^a TTT, tetrathiatetracene; HMTSF, hexamethylenetetraselenafulvalene, TCNQ, tetracyanoquinodimethane; KCP, $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 2.3\text{H}_2\text{O}$. ^b Hilti, B.; Mayer, C. W. *Helv. Chim. Acta* 1978, 61, 501. ^c Bloch, A. N.; Cowan, D. O.; Bechgaard, K.; Pyle, R. E.; Banks, R. H.; Poehler, T. O. *Phys. Rev. Lett.* 1975, 34, 1561. ^d Thomas, G. A.; Schafer, D. E.; Wudl, F.; Horn, P. M.; Rimai, D.; Cook, J. W.; Glocker, D. A.; Skove, M. J.; Chu, C. W.; Groff, R. P.; Gillson, J. L.; Wheland, R. C.; Melby, L. R.; Salamon, M. B.; Craven, R. A.; De Pasquali, G.; Bloch, A. N.; Cowan, D. O.; Walatka, V. V.; Pyle, R. E.; Gemmer, R.; Poehler, T. O.; Johnson, G. R.; Miles, M. G.; Wilson, J. D.; Ferraris, J. P.; Finnegan, T. F.; Warmack, R. J.; Raaen, V. F.; Jerome, D. *Phys. Rev. B* 1976, 13, 5105.

free path⁸ along the stacking direction, λ_{\parallel} , to the intermolecular spacing, d

$$\bar{\lambda} = \lambda_{\parallel}/d = hA\sigma_{\parallel}/(4e^2d) \quad (3)$$

where h is Planck's constant, A is the cross-sectional area per conducting stack, and e is the electronic charge. A value for $\bar{\lambda}$ of less than unity is indicative of diffusive or hopping motion of the charge carriers, while a value of $\bar{\lambda}$ greater than unity is associated with a wavelike mechanism for the conductivity. As can be seen in Table II, the three isostructural and isoionic large-ring metallomacrocycles, Ni(tbp), Ni(tatbp), and Ni(pc), and the small-ring metallomacrocycle Ni(tmp)I as well, have room-temperature values of $\bar{\lambda}$ in the range $\bar{\lambda} \sim 1$, the nominal crossover point from diffusive to wavelike motion. At lower temperature a distinctly wavelike behavior emerges, with $\bar{\lambda} \sim 10$ -20 in some cases.

If one examines the Ni-Ni separations in Table I it is not surprising that Ni(omtpb)I has the lowest conductivity and smallest $\bar{\lambda}$ of the M(p)I complexes listed in Table II. With a Ni-Ni distance of 3.778 Å we would expect poor intermolecular overlap and a small value for the electron-transfer matrix element, t . Indeed, magnetic susceptibility measurements allow us to set a limit of $t < 3 \text{ cm}^{-1}$.¹⁸ Nevertheless Ni(omtpb)I exhibits a metal-like conductivity at room temperature (Figure 2) comparable with that of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 2.3\text{H}_2\text{O}$ (KCP, or Krogmann's salt).^{1-3,6} Since charge transport in KCP occurs along a spine of closely spaced platinum atoms (Pt-Pt = 2.90 Å), the results for Ni(omtpb)I clearly demonstrate the overriding importance of the nonintegral oxidation state in obtaining ready charge transport in molecular crystals.

Intrastack Interactions vs. Intermolecular Correlations

The high conductivities exhibited by these materials must be a reflection of the interactions between adja-

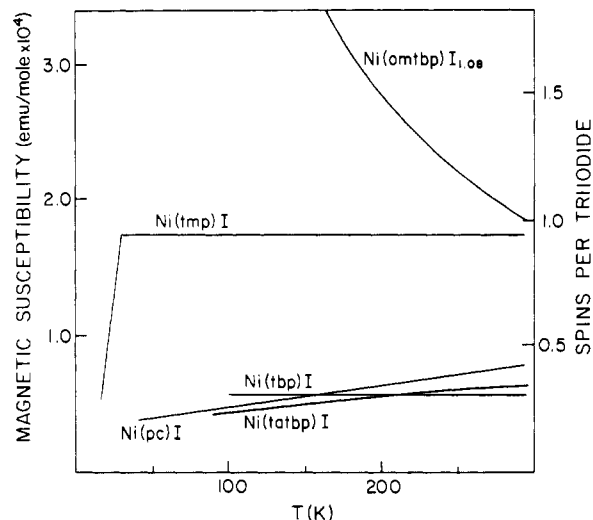


Figure 5. Temperature responses of spin susceptibilities of several porphyrinic molecular conductors. References are in the text. Typical uncertainties are $\pm 10\%$ of the indicated values.

cent molecules along a stack, and these may be probed by measuring the paramagnetic susceptibility (integrated EPR intensity) associated with the carrier spins. The materials prepared from the flat, unsubstituted large-ring porphyrinic macrocycles Ni(pc) and Ni(tbp) have a room temperature spin susceptibility, χ^s , that corresponds to ~ 0.1 spin per macrocycle, strongly reduced from what would be observed if each oxidized macrocycle (one per three sites) were an independent paramagnet. Furthermore, χ^s is at most weakly temperature dependent (Figure 5). These characteristics, which are similar to those of the susceptibility of a metal, suggest that these substances might be described in first approximation by the simplified tight-binding picture of a one-dimensional metal. In this model the susceptibility is low and approaches temperature independence when the interaction between molecules becomes large, with the calculated susceptibility being proportional to t^{-1} (β^{-1}).⁸ Application of this model to the room-temperature susceptibility of these M(L)I materials shows that intermolecular interactions along a M(L) stack are appreciable, $|t| \sim 800 \text{ cm}^{-1}$, consistent with the extensive intermolecular contacts in the crystal structures. Thermodynamic studies employing solid-state electrochemical cells show that these interactions could play a significant role in stabilizing the mixed-valence solid.¹⁶

The spin susceptibility of Ni(tmp)I is also temperature independent down to a transition temperature of 28 K, well below the conductivity maximum (Figure 5). At temperatures below the transition the susceptibility decreases in an activated fashion. The model of a one-dimensional tight-binding band of noninteracting electrons is not able to describe the susceptibility of Ni(tmp)I for $T > 28 \text{ K}$. Although χ^s is temperature independent, which indicates strong interactions between macrocycles, the room-temperature paramagnetism corresponds to $\sim 1/3$ spins per macrocycle, the value expected for noninteracting spins. The failure of the model to describe the behavior of Ni(tmp)I most probably arises from neglect of electron correlation effects. Within the context of one-electron molecular orbital theories this problem is well-known to chemists as overemphasis of ionic states.⁴² the many-electron

tight binding wave function not only includes terms with oxidized $[\text{Ni}(\text{L})]^+$ and neutral $\text{Ni}(\text{L})$ molecules but also has large contributions from doubly oxidized $[\text{Ni}(\text{L})]^{2+}$ sites. Such a dicationic site is unfavorable by roughly the difference between the first and second ionization (or redox) potentials of $\text{Ni}(\text{L})$. This disproportionation energy is equivalent to a repulsion energy between holes and is usually given the symbol U .^{26,27} Inclusion of U in the theory has the effect of reducing the importance of dicationic contributions to the crystal wave function, and this increases the Pauli susceptibility because the suppressed terms involve the diamagnetic, closed shell $[\text{Ni}(\text{L})]^{2+}$ dication. Within the physics literature this effect is called "Coulomb enhancement" of the susceptibility.⁴

The striking threefold increase in the susceptibility of $\text{Ni}(\text{tmp})\text{I}$ over that of, say, $\text{Ni}(\text{pc})\text{I}$ can be readily understood in terms of larger correlation effects, a larger value of U/t , for the small-ring compound. This probably reflects a smaller t , a consequence of the large interplanar spacing within a $\text{Ni}(\text{tmp})$ stack (Table I). It may also indicate that the disproportionation energy, U , is larger in $\text{Ni}(\text{tmp})\text{I}$ than in the large-ring systems, where charge delocalization is more facile. A mechanism that involves the $[\text{Ni}(\text{tmp})]^{2+}$ triplet state has also been discussed.²⁰

The limiting condition of nonzero t but $4t/U \rightarrow 0$ is called the "atomic limit" because it represents the case of extremely weak interaction between subunits.^{43,44} In this limit terms in the crystal wavefunction involving the $[\text{Ni}(\text{L})]^{2+}$ dication are of negligible importance. The appropriate description of a partially oxidized stack is then in terms of a valence-bond type wave function, in which the charge of each site is specified and can be only 0 or 1+. In this limit the carriers on a nonintegrally oxidized chain are still free to move by jumping from one site to another, while the spins associated with the carriers behave as though they interact by an antiferromagnetic exchange interaction of magnitude $J \sim 4t^2/U$. The atomic limit is realized with $\text{Ni}(\text{omtbp})\text{I}$.^{18,19} The susceptibility of $\text{Ni}(\text{omtbp})\text{I}$ has a Curie-law temperature dependence down to 15 K, with a magnitude that indicates that each oxidized macrocycle (one per three sites) acts as an independent paramagnet. This result requires that any exchange interaction between spins be less than a few wavenumbers and that the matrix element for charge transfer along a $\text{Ni}(\text{omtbp})$ stack must be small, less than 3 cm^{-1} . Clearly, this weak interaction is a consequence of poor intermolecular contact between the $\text{Ni}(\text{omtbp})$ building blocks, as reflected in the large Ni-Ni spacing (Table I). A joint analysis of the EPR spectra and conduction of the crystals shows that these properties can be understood in terms of paramagnetic $[\text{Ni}(\text{omtbp})]^+$ sites and correlated one-dimensional hopping of carriers (polarons), very much a realization of the situation represented in Scheme III.¹⁹

Thus we see that $\text{Ni}(\text{pc})\text{I}$, $\text{Ni}(\text{tmp})\text{I}$, and $\text{Ni}(\text{omtbp})\text{I}$ form an isoionic series in which Coulomb correlations (U) are of progressively greater importance relative to the charge-transfer interactions (t) and that the relative importance of the correlation can be modified in an understandable fashion through controlled changes in

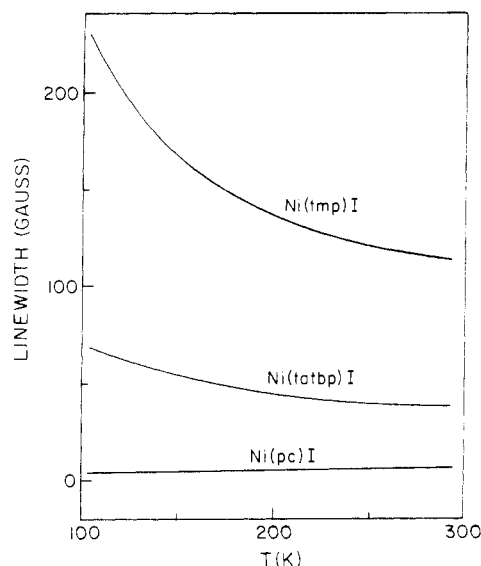


Figure 6. Temperature responses of the carrier-spin EPR line widths for three isostructural, large ring $\text{M}(\text{L})\text{I}$ crystals. (Uncertainties $\pm 10\%$.) References are in the text.

the metallomacrocycle building blocks. The large-ring systems, such as $\text{Ni}(\text{pc})\text{I}$ of Table I, at least to first approximation, appear to be usefully discussed with the simple construct of a tight-binding metal with delocalized states and wavelike conduction, as suggested by the metallic conductivity as $T \rightarrow 0 \text{ K}$. On the other hand, charge transport in $\text{Ni}(\text{tmp})\text{I}$ is more diffusive, and here Coulomb correlations play a major role in determining the magnetic properties. Finally, $\text{Ni}(\text{omtbp})\text{I}$ represents the limiting case where the appropriate picture is that of localized holes that hop between sites, very much as in Scheme III.

Doubly Mixed Valency

The charge-carrying hole species produced by partial oxidation of the $\text{M}(\text{L})$ complexes may themselves be characterized by examining the g values and line widths of their EPR signals. This process allows us to discriminate among possible modes of oxidation, such as the limiting case in which electron loss occurs from metal (eq 1) or from ring (eq 2). For the majority of the porphyrinic $\text{M}(\text{p})\text{I}$ compounds of Table I the g values are temperature independent and very near to the free electron value ($g_e = 2.002$) and the EPR line widths (Γ) are relatively small ($\sim 5 \text{ G}$ at room temperature) and depend weakly on temperature (Figure 6). Analysis of the g values shows that in such cases (for example $\text{Ni}(\text{pc})\text{I}$,¹¹ $\text{Ni}(\text{omtbp})\text{I}$,^{17,18} and $\text{Ni}(\text{tmp})\text{I}$,²⁰) the charge carriers created by partial oxidation are ligand based, with only a small contribution from iodine. Thus the metal does not contribute directly to the carrier orbital or charge transport process and acts solely as an internal substituent that influences the electronic properties of the ring.

In contrast, the carrier spin g values and line widths for $\text{Ni}(\text{tbp})\text{I}$ are unusually large at room temperature ($g_{\text{av}} = 2.03$, $\Gamma = 105 \text{ G}$) and increase strongly as the temperature is lowered (Figure 6). Similar observations have been made for $\text{Ni}(\text{tatbp})\text{I}$. Moreover, the EPR line widths show an unprecedented increase with increasing spectrometer frequency.¹⁵ This may be contrasted with the frequency-independent line widths of $\text{Ni}(\text{pc})\text{I}$, $\text{Ni}(\text{omtbp})\text{I}$, and, for example, TTF-TCNQ. These ob-

(43) Beni, G.; Holstein, T.; Pincus, P. *Phys. Rev. B* **1973**, *8*, 312.

(44) Klein, D. J., *Phys. Rev. B* **1973**, *8*, 3452.

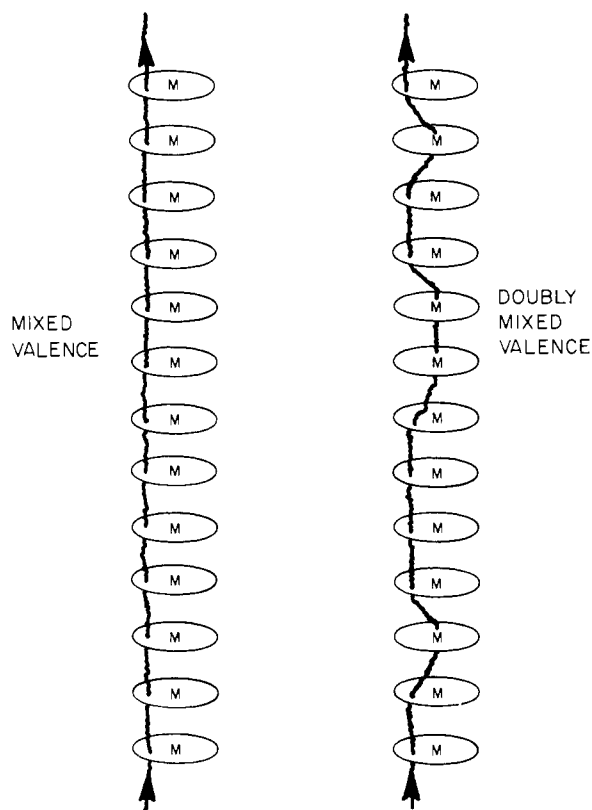


Figure 7. Schematic representation of carrier motion on a nonintegral oxidation state metallomacrocycle stack. Left: Mixed valence system created by partial oxidation of the ring. Right: Doubly mixed valence stack in which the carriers formed by partial oxidation of $M(L)$ can hop between ligand and metal.

servations require that the oxidation no longer be purely ligand based, but instead be of a mixed ligand- π and metal-d character. For example, interpretation of the room-temperature g values of $Ni(tbp)I$ requires a contribution of ca. one-fifth from the $[Ni^+(tbp)]$ form of the oxidized parent macrocycle. Thus, these compounds show characteristics intermediate between those of the metal-spine conductors and the organic conductors.

Detailed considerations of the EPR results indicate that the carrier is *not* delocalized in an orbital encompassing both ligand and metal, but rather that the electron holes created by iodine oxidation have either one identity or the other and hop between ligand and metal. Moreover, they do so with a frequency ω_i that

is lower than the intermolecular hopping rates associated with the conducting process, but is comparable with the difference between the resonance frequency for a pure metal ion d spin and a pure ligand π radical: $\omega_i \sim 10^9$ – 10^{10} s^{-1} . In chemical terms, the intermolecular mixed valency involving the mobile holes along a $Ni(L)I$ stoichiometric formula as $[Ni(L)]_2[Ni(L)]^+(I_3^-)$. In addition, the $[Ni(tbp)]^+$ and $[Ni(tatbp)]^+$ cations exhibit an intramolecular mixed valency or electronic tautomerism, with interconversion between $[Ni^+(L)]$ and $[Ni(L)^+]$ forms. Thus, as shown schematically in Figure 7, these complexes exhibit a novel electronic structure that we have called^{14,15} a doubly mixed valence state.

Concluding Remarks

Because of the high and anisotropic conductivities and unusual carrier properties of the metallomacrocycle systems with nonintegral oxidation states we expect that major efforts in the near future will focus on their preparation and characterization. Far less effort has gone into the study of these new systems than of organic metals, although we find that the metal-containing systems, as typified by the metalloporphyrins, exhibit most of the features of importance and interest observed in their organic counterparts. These metal complexes offer the very important advantage of chemical flexibility that enables the fine-tuning of the relative energy of metal and ligand orbitals, and hence potential control of the physical properties. We anticipate a successful correlation of structures with physical properties that will accelerate the synthesis and utilization of this class of materials.

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