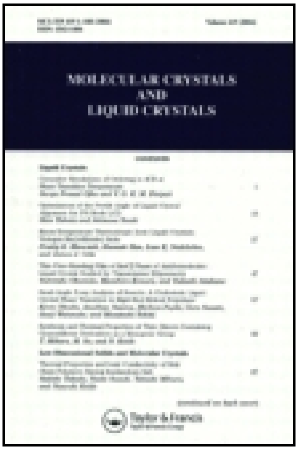

Molecular Crystals and Liquid Crystals

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Porphyrinic Molecular Metals

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PORPHYRINIC MOLECULAR METALS

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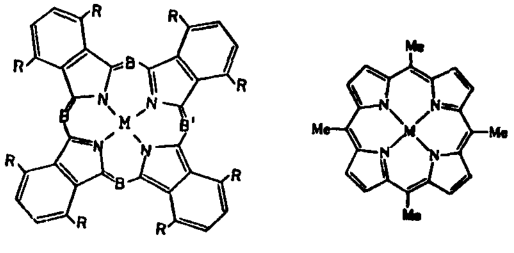
Abstract Porphyrinic molecular metals rival the organic metals in the range of their properties and surpass them in the tunability of these properties. Such tunability is illustrated here by the changes that occur in M(L)X systems upon change of ligand L or metal M or oxidant X. Among the compounds thus produced are Ni(pc)I, the first low-temperature molecular metal that does not contain a chalcogen, and Co(pc)I, the first metal-spine conductor not based on a Pt complex.

INTRODUCTION

Highly conducting molecular crystals may be obtained by partial oxidation of metallomacrocycles. Such systems, prepared from porphyrin and phthalocyanine complexes, may be viewed as derivatives of the metalloporphine 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)

M(tmp)

FIGURE 1 Relevant metallomacrocycles.

Partial oxidation of these metalloporphyrins yields materials with highly anisotropic physical properties, including metallic conduction in one dimension.[1]

The extreme chemical flexibility of these metal-ligand complexes permits systematic alterations of their electronic structure, through either metal substitution or ligand modification, without affecting the basic structural motif in the solid state. In contrast, the Krogmann salts are not amenable to chemical modification;[2] such alterations in the organic conductors often produce profound changes in both the structure and degree of charge transfer.[3] Thus only in the porphyrinic systems are we able to correlate physical properties of these highly conducting materials with the steric and electronic properties of the subunits. The existence of the metal-organic framework in these compounds affords conduction pathways that may involve either the metal spine or the ligand π-orbitals or both. In addition, the availability of a number of potential oxidants makes further modification of these systems possible.

Here we summarize some earlier results from this laboratory and provide new data on these porphyrinic molecular metals that illustrate not only their chemical flexibility but also their wide range of physical properties.

CHANGE OF LIGAND (L) IN Ni(L)I SYSTEM

The basic structure of the Ni(L)I systems is illustrated for Ni(pc)I[4] (Figure 2). The Ni(pc) units stack on top of one another with the two molecules in the unit cell rotated with respect to one another by about 40°. Iodine, identified primarily as I_3^- from spectroscopic studies, fills the channels between the stacks of metallomacrocycles.

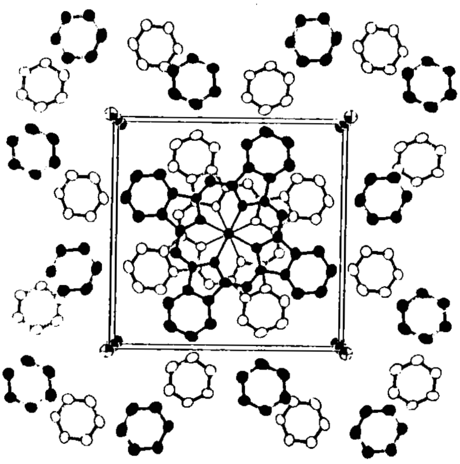


FIGURE 2 View down the c axis of the unit cell of Ni(pc)I. Hydrogen atoms are omitted.

Table I provides metrical data for these systems. From Table I it follows that change of the ligand L brings about significant changes in the Ni-Ni intrastack distance in Ni(L)I systems. These changes are strikingly reflected in physical properties, as illustrated in Figure 3 for the temperature dependence of the conductivity along the stacking axis.

Ni(pc)I[4,5] is the most extensively studied M(L)I compound. Its conductivity is high and metal-like (Figure 3); its mean-free carrier path is consistent with a wavelike conductivity mechanism. The charge carriers are associated solely with ligand orbitals, rather than with those of the metal. Ni(pc)I is therefore an organic conductor that may be accurately described in terms of the tight-binding picture of a one-dimensional metal. The conductivity of

TABLE I Metrical data and room-temperature conductivities for some M(L)X compounds.

Compound	M-M Inter-stack (Å)	M-M Intra-stack (Å)	T (K)	σ(25°C) $\Omega^{-1}cm^{-1}$	Ref.
Ni(pc)I	13.94(1)	3.244(2)	298	500	4,5
Ni(tmp)I	11.75(1)	3.466(3)	114	110	6,7
Ni(omtbp)I	14.86(1)	3.778(3)	298	10	7,8
Ni(tbp)I	14.08(2)	3.217(5)	113	330	7,9
H_2(pc)I	13.91(2)	3.205(5)	97	750	10
Cu(pc)I	13.89(1)	3.195(4)	97	900	11
Co(pc)I	13.93(1)	3.123(1)	116	50	13
Fe(pc)I*	13.84(2)	3.39(1)	97	20	14
Ni(pc)Br	13.79(1)	3.216(2)	167	160	10

*Fe(pc)I forms crystals of very low quality and the compound will not be discussed further here.

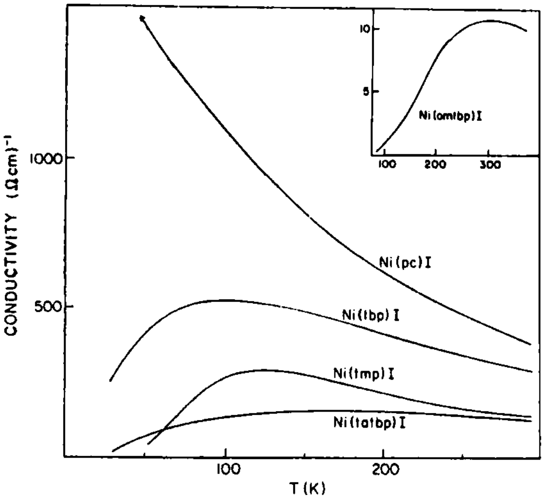


FIGURE 3 Temperature dependence of the conductivity along the stacking axis for some Ni(L)I systems.

Ni(pc)I increases with decreasing temperature to 30 K; it remains highly conductive to 100 mK, the lowest temperature examined.[5] Epr, thermoelectric power, and magnetic measurements at low temperature confirm that the metallic band structure is maintained to below 2 K. Thus Ni(pc)I is the first low-temperature molecular metal that does not contain chalcogens.[5]

The compounds Ni(tmp)I[6,7] and Ni(omtbp)I[7,8] are isoionic with and adopt the same structural motif as Ni(pc)I, but they show very different physical properties. Whereas Ni(pc)I is a low-temperature molecular metal, both Ni(tmp)I and Ni(omtbp)I show conductivity behavior that is more characteristic of many quasi one-dimensional systems (Figure 3). Again the carriers are ligand based. The small-ring conductor, Ni(tmp)I, has a longer intrastack spacing than Ni(pc)I and its conductivity is better described by a hopping or diffusive mechanism. As the intrastack spacing increases and the extent of delocalization of charge within the plane decreases, Coulomb interactions become more important, as verified by magnetic susceptibility measurements. The intrastack spacing in Ni(omtbp)I is longer still, and this compound is the least conductive of the Ni(L)I materials. It too displays a diffusive mechanism for charge transfer. Despite the long intrastack spacing its room-temperature conductivity is metal-like and comparable with that of Krogmann's salt. For Ni(omtbp)I Coulomb correlations dominate and the "atomic limit" is realized -- Ni(omtbp)I represents the limit of extremely weak interactions between molecular subunits. Indeed, the magnetic susceptibility is Curie-like, indicative of localized spins. Thus Ni(pc)I, Ni(tmp)I, and Ni(omtbp)I form an isoionic series in which

Coulomb correlations are of progressively greater importance relative to charge transfer interactions. Note that we can modify the relative importance of correlation effects in an understandable fashion through controlled changes in the metallomacrocycle building blocks.

Comparison of the compounds Ni(tbp)I[7,9] and Ni(tatbp)I[7] with Ni(pc)I illustrates how subtle variations in the electronic framework of the ligand can affect the nature of the charge carriers in isostructural systems. Ni(tbp)I and Ni(tatbp)I are the first molecular metals in which the charge carriers exhibit both metal and ligand properties. Rather than having the conduction electrons confined to π-orbitals of organic moieties or the d-orbitals of metal atoms in a chain, partial oxidation creates electron hole species that exist on both the Ni and L sites. The charge carriers are localized on the ligand or metal sites and can hop between them with a frequency that is lower than the intermolecular hopping rate associated with the conduction process. Thus these compounds exhibit a novel "doubly mixed valent" state.

CHANGE OF METAL IN M(pc)I SYSTEMS

Just as the change of ligand L in the Ni(L)I systems strikingly affects their physical properties, the change of metal, M, illustrated here for M(pc)I systems, brings about equally striking but different effects. Upon change of metal, the electronic environment of the macrocycle is altered and the band structure may change. There may also be a shift in oxidation potential of the metallic center. But, as evidenced by Ni(pc)I, the metal need take no direct part in the conduction process; indeed, H_2(pc)I is as highly conductive as some metal derivatives.[10]

Some structural data on M(pc)I systems are shown in Table I. Note the wide variation in intrastack spacings. Coulomb correlations are of progressively greater importance relative to charge transfer interactions. Note that we can modify the relative importance of correlation The structures are similar and yet the simple chemical modification of change of metal brings about significant differences in the conductivities of these compounds, as illustrated in Figure 4.

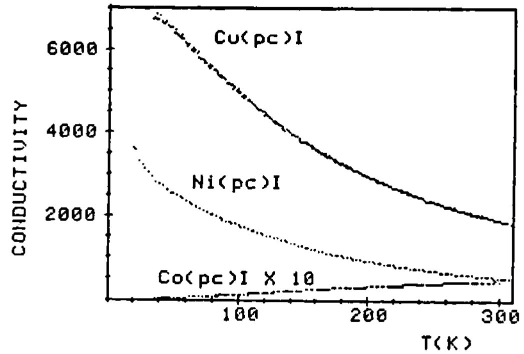


FIGURE 4 Conductivities of selected M(pc)I systems.

Ni(pc)I is a purely π-conductor. Replacement of the diamagnetic Ni^{2+} by paramagnetic Cu^{2+} centers leaves the conduction mechanism unchanged but introduces important differences. Magnetic susceptibility, epr, and thermoelectric power measurements show that Cu(pc)I[11] is metallic down to 40 K, the lowest temperature examined. The principal charge carriers are holes associated with the ring and the Cu centers remain Curie-like. Thus the novel feature of this compound is that it contains a dense (1/site) system of Cu^{+2} ($S=1/2$) local spins interacting with each other and with a "Fermi sea" of itinerant carriers. Equally interesting, the single exchange-coupled epr signal of Cu(pc)I abruptly broadens and vanishes at about 8 K while the static susceptibility is only slightly perturbed, suggesting a transition, perhaps to a spin-density wave state, that involves both spin systems.[12]

Although Co^{+2} also has an unpaired local spin the conductivity of Co(pc)I[13] clearly is very different from that of its Ni or Cu analogues (Figure 4). Moreover, the sign of the thermoelectric power is negative, identifying electrons as the charge carriers. The valence band formed in the Co(pc) stack would be only half-filled and oxidation by 1/3 electrons per site yields a band that is 1/3 filled; thus conduction is associated with electrons and the conductive pathway is along the Co spine. Co(pc)I is the first metal-spine conductor that is not based on a Pt complex. Furthermore, the room-temperature conductivity of about 50 $\Omega^{-1}cm^{-1}$ is comparable with other metal spine conductors, despite the fact that the Co-Co distance of 3.12 Å is much greater than the typical Pt-Pt distance of 2.95 Å. The conductivity of Co(pc)I decreases almost linearly with decreasing temperature; this seems to reflect the strong one-dimensional character of charge transport along highly isolated chains of Co atoms.

Figure 5 is a representation of the strikingly different conductivity pathways for the isostructural and isoionic compounds Ni(pc)I, Cu(pc)I, and Co(pc)I. Simple metal substitution has resulted in shifting the mechanism of charge transport from simple π-overlap to π-overlap modulated by interactions with the metal site to M-M overlap.

CHANGE OF OXIDANT IN Ni(pc)X SYSTEMS

The choice of oxidants is not limited to I_2. Since Br_2 is a better oxidant than I_2 and is smaller, there is the possibility that oxidation with Br_2 may produce a compound with structure or conductivity different from that of its iodine analogue.

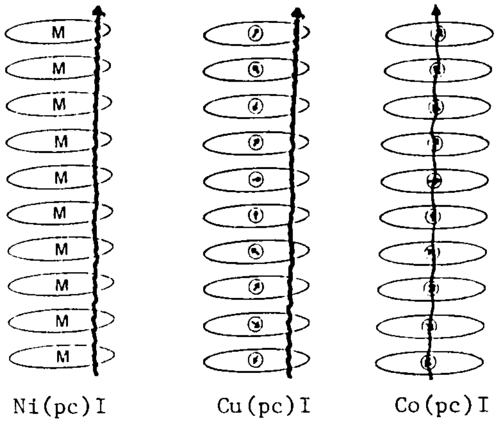


FIGURE 5 Schematic representation of conductivity pathways in some M(pc)I systems.

Our first experiment with Br_2 as an oxidant has yielded a very interesting result. Ni(pc)Br[10] is isostructural with Ni(pc)I (Table I) and contains Br_3^- species. Despite these similarities the conductivity of Ni(pc)Br differs markedly from that of Ni(pc)I (Figure 6). We have not yet determined the conductivity behavior below 100 K. To a first approximation the magnetic susceptibility and epr characteristics of the two compounds are very similar. Since theoretical descriptions of M(L)X systems generally concentrate on the M(L) portion and ignore, in first approximation, the effects of X, these results on Ni(pc)I and Ni(pc)Br seem especially provocative.

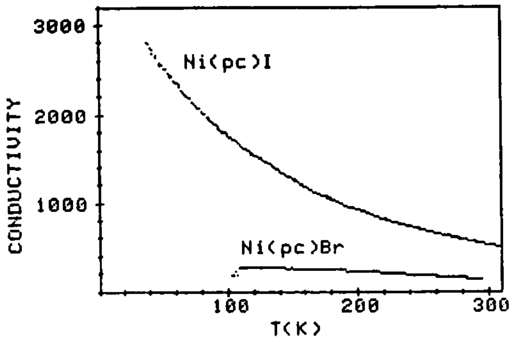


FIGURE 6 Conductivity behavior for Ni(pc)I and Ni(pc)Br.

CONCLUSION

We have outlined the profound changes in physical properties that occur in M(L)X systems upon deliberate change of M or L or X. Such changes are readily made in these chemically malleable systems, far more readily than in the more widely studied organic metals. Yet these porphyrinic molecular metals show most of the features of the organic metals. We believe that continued study of these porphyrinic molecular metals nicely complements studies of organic metals and will contribute substantially to the mutual goal of designing materials with specific physical properties.

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