

# One-dimensional coordination polymers: Applications to material science\*

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## ABSTRACT

Coordination metal complexes with one-dimensional polymeric structures have long been investigated as materials with unusual properties. Molecular-based ferromagnets, synthetic metallic conductors, non-linear optical materials, and ferroelectrics represent several applications of low-dimensional coordination polymers. It is possible to modify the bulk magnetic, electrical, and optical properties of such materials by tailoring the constituent molecules. This review presents recent examples of each of these applications and focuses on the correlation between the molecular structure and the bulk properties of the materials.

## 1. INTRODUCTION

Nearly 30 years ago, John C. Bailar, Jr. drew an analogy between organic polymers and a class of inorganic coordination complexes that he called "coordination polymers" [1(a)]. His seminal review described and classified the synthesis and structures of inorganic chain compounds. Since that time, one-dimensional coordination polymers of metal complexes have been intensely studied [1]. The fundamental chemistry and physics behind their fascinating structures have stimulated interest in their possible uses as unusual materials for new technologies.

\* Dedicated to the memory of Professor John C. Bailar, Jr.

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The electrical, optical, and magnetic properties of coordination polymers are a complex function of their chemical, electronic, and architectural structures. Bridging the gap between molecular characteristics and bulk properties remains a continuing challenge to both the chemical and material sciences. In the structures of one-dimensional coordination polymers, the well-defined cooperative interactions between discrete molecules provide a continuum between these fields.

Molecular-based ferromagnets, synthetic-metal conductors, non-linear optical (NLO) materials, and ferroelectric materials are among the most important applications of such coordination polymers. This review will examine newly developed one-dimensional coordination compounds in each of these areas. We will not attempt to be comprehensive, but rather we will focus on the correlation between the polymer structures and their bulk material properties.

## 2. MOLECULAR FERROMAGNETS

In the 1980s, several prototypes of the light-weight “molecular magnets” emerged, based on one-dimensional coordination polymers [2]. These *molecular-based* magnets are in contrast to the traditional atom-based inorganic magnetic materials. Antiferromagnetism, ferrimagnetism, and ferromagnetism all originate from the cooperative behavior of magnetic spins within a solid. For molecular-based magnets, an appropriate molecular structure must be designed to avoid the antiferromagnetic (i.e. anti-aligned) coupling of spin centers [3]. To design molecular materials displaying a zero-field magnetization below some critical temperature  $T_c$ , one must assemble paramagnetic molecular units so that the interaction between the local spin carriers results in a non-zero spin on the bulk material scale. This can be achieved under various conditions, as shown schematically in Fig. 1. In class (i), two aligned ferromagnetic chain structures are formed. In (ii), two ferrimagnetic chains are shown where the coupling between unequal spin centers is antiferromagnetic, resulting in a net non-zero spin between centers. In (iii), all the spin carriers are similar and couple antiferromagnetically, but a small canting causes a net spin. Finally, in (iv), a non-zero spin arises from more complicated spin structures involving both ferromagnetic and antiferromagnetic couplings, with canting as an additional possibility.

At first glance, one might expect antiferromagnetic and ferromagnetic coupling to be equally likely. However, less than 5% of well-characterized dinuclear complexes have been reported to be ferromagnetically coupled [4(a)]. Ferromagnetic coupling results only if the state of high-spin multiplicity is more stable than that of low-spin multiplicity. A general strategy to achieve the ferromagnetic coupling between two spin centers is to make the magnetic orbitals of adjacent centers orthogonal. This proves to be a synthetically difficult task [4(b),(c)]. Alternatively, the propensity for antiferromagnetic coupling means that building a ferrimagnetic chain structure with a non-compensated net magnetic spin is synthetically easier [4(d)]. In this review,

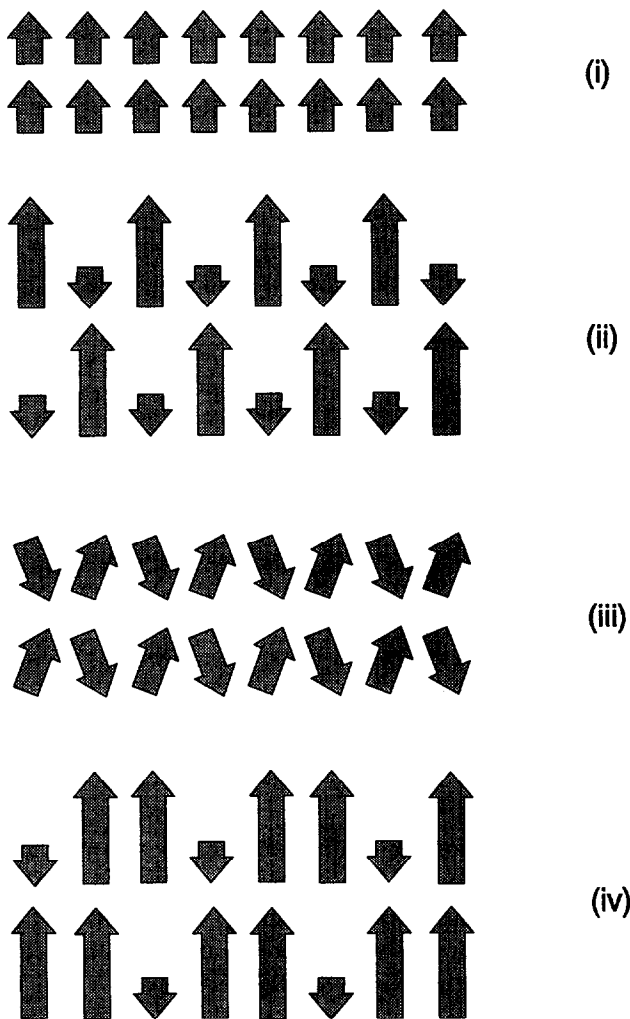


Fig. 1. Schematic representations of non-zero magnetization of two-dimensional arrays of spins.

we will concentrate on two types of class (ii) ferrimagnetic coordination polymers: metal–radical and ordered biheterometal structures.

The first approach is represented by the work of Gatteschi and co-workers on metal complexes of nitronyl oxides, the 2-substituted-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (NIT-R in Fig. 2) [5]. With one stable unpaired electron delocalized over two equivalent N–O groups, NIT-R can form linear chains by bridging two individual metal complexes: for example,  $[M(\text{hfac})_2(\text{NIT-R})]_{\infty}$  derives from  $M(\text{hfac})_2$ , where M is Mn(II), Ni(II), or Cu(II) and hfac is hexafluoroacetylacetonate (Fig. 2). The magnetic properties of these polymer chains can be either ferromagnetic (as with Cu(II)) or alternating-spin ferrimagnetic (as with Mn(II) or Ni(II)). The nitronyl

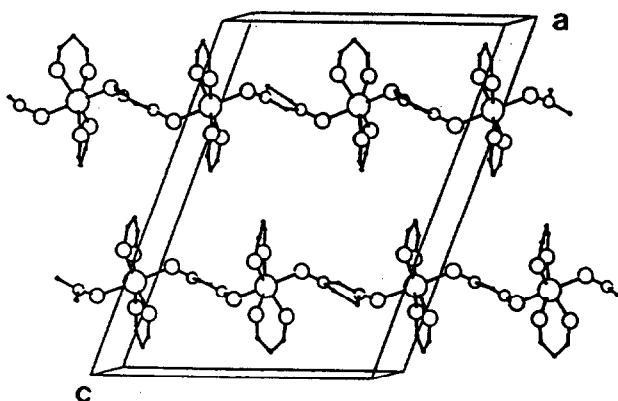
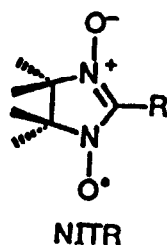


Fig. 2. The unit cell of  $[\text{Mn}(\text{hfac})_2(\text{NIT-i-Pr})]_\infty$ . The  $\text{CF}_3$  and  $\text{CH}_3$  groups have been omitted [5(c)].

oxides not only act as the bridging ligand for the chain structure but also provide the unmatched spin. This leads to non-compensated net moments after antiparallel alignment with those of metal ions. The manganese and nickel compounds were shown to undergo a transition, presumably driven by the dipolar interaction between chains, to three-dimensional ferromagnets at ca. 8 and 5 K, respectively.

The ordered biheterometal approach is illustrated by the work of Kahn and co-workers [6]. They used Cu(II) complexes of the diamagnetic ligand 1,3-propylenebis(oxamate) and its 2-hydroxy derivative (pba and pbaOH, respectively) as the building blocks for the polymeric chains (Fig. 3). The two sets of  $\alpha$ -dicarbonyl groups on  $[\text{Cu}(\text{pba})]^{2-}$  and  $[\text{Cu}(\text{pbaOH})]^{2-}$  can coordinate to different metal ions, thus forming equally spaced biheterometallic chains. If Mn(II) or Ni(II) ions are coordinated to the Cu complex, then the two local spins ( $S=1/2$  of Cu(II) vs.  $S=5/2$  of Mn(II) or  $S=1$  of Ni(II)) will be non-compensable even with antiferromagnetic coupling. It has been shown that a spontaneous ferromagnetic magnetization occurs in  $[\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3]_\infty$  at ca. 5 K.  $[\text{MnCu}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}]_\infty$ , however, orders antiferromagnetically at 2.2 K. Although these compounds have very similar chain structures, the relative positions of the chains within the lattice are slightly different (Fig. 3). Displacement of every other chain in the  $b$  direction leads to

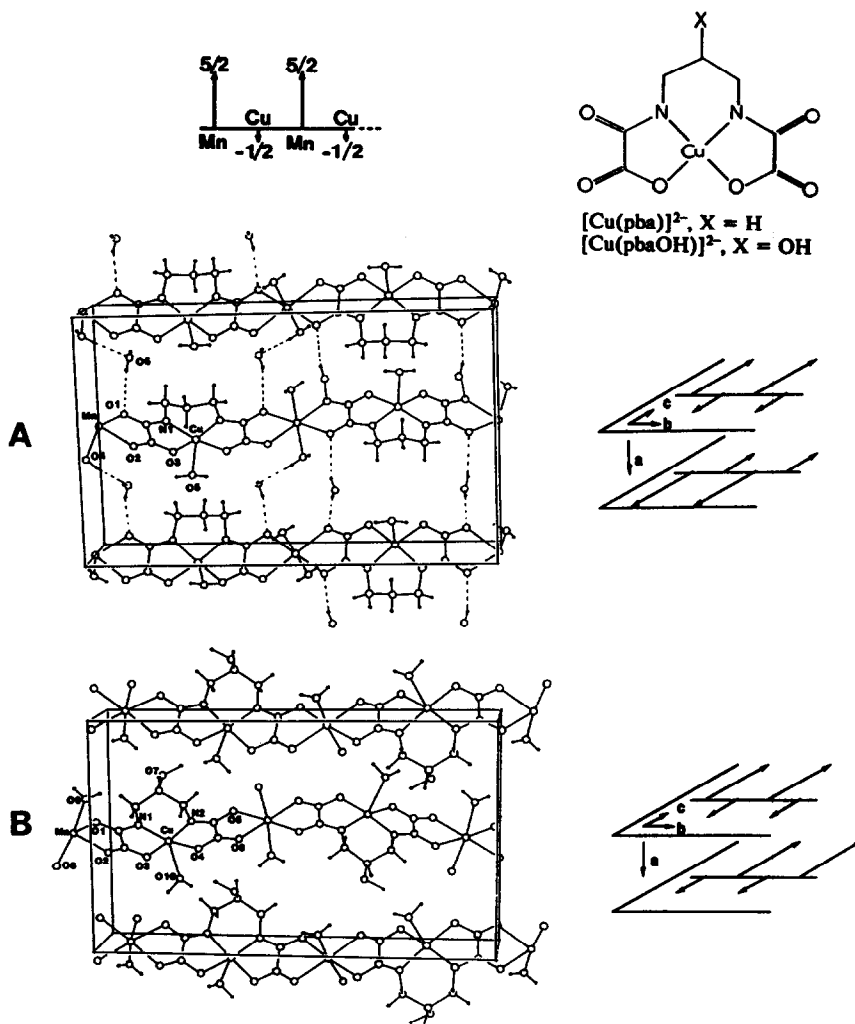


Fig. 3. Three neighboring chains in  $[\text{MnCu}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}]_\infty$  (A), and in  $[\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3]_\infty$  (B). Their magnetic spin topologies are shown schematically on the right [6(b),(d)].

completely different magnetic properties at low temperature. Ferromagnetic interchain interactions are created by imposing  $\text{Mn} \cdots \text{Cu}$  instead of  $\text{Mn} \cdots \text{Mn}$  and  $\text{Cu} \cdots \text{Cu}$  as the shortest interchain separation.

Since ferromagnetism is a three-dimensional property,  $T_c$  in one-dimensional polymers will depend on the magnitude of both intra- and interchain interactions. While the former interaction may be large, the latter are weak since they are essentially dipolar interactions. Consequently, the critical temperatures of these one-dimensional compounds are generally below 10 K. The different interchain inter-

action (antiferromagnetic vs. ferromagnetic ordering), caused by the subtle relative position between the polymeric chains in  $[\text{MnCu}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}]_\infty$  and  $[\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3]_\infty$ , clearly illustrates the importance of interchain interaction. To increase  $T_c$  substantially, it is necessary to develop new materials which have strong interactions in all three dimensions [7].

In several cases, increasing the dimensionality of the interaction can raise the critical temperature of spontaneous magnetization. Recently, the critical temperature of  $[\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3]_\infty$  has been raised to 30 K (a record for molecular-based magnetic materials) by thermally removing the coordinated water molecules [6(d)]. Examination of the structure of  $[\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3]_\infty$  suggests that the separation along the *a* axis is partially controlled by an apical water molecule weakly bound to copper ( $\text{Cu}-\text{O}=2.417 \text{ \AA}$ ). It has been proposed that the selective elimination of these water ligands causes the chains to be closer to each other and subsequently enhances the interchain interaction.

This approach does not always succeed in giving large  $T_c$  values, however. Coronado and co-workers [8] studied the magnetic properties of the bimetallic compounds of the EDTA family formulated as  $\text{MM}'[\text{M}(\text{EDTA})]_2 \cdot 4\text{H}_2\text{O}$ . These compounds can be thought of as ordered bimetallic layers of alternating chelated and hydrated metal ions in octahedral and tetrahedral sites. The cross-linking between chains through carboxylate bridges increases the dimensionality of the system. In spite of this, the  $T_c$  values of the complexes of Co, Zn, and Ni are very small,  $<1.0 \text{ K}$  [8(e)].

Another method to increase the magnetic interaction between chains is to build a three-dimensional network through covalent connections. Gatteschi and his co-workers [5(e)] have tested this on the  $[\text{M}(\text{hfac})_2(\text{NIT-R})]_\infty$  system with a tridentate ligand NIT-pPy, i.e. R=4-pyridyl. The crystal structure of  $[\text{Cu}(\text{hfac})_2]_3(\text{NIT-pPy})_2$  (Fig. 4) shows that one-dimensional polymer chains are still formed. These chains consist of dimeric units,  $[\text{Cu}(\text{hfac})_2(\text{NIT-pPy})]_2$ , which are bridged by  $\text{Cu}(\text{hfac})_2$  molecules. Magnetic studies indicated that  $[\text{Cu}(\text{hfac})_2]_3(\text{NIT-pPy})_2$  behaves as a one-dimensional antiferromagnetic chain material. The same tridentate ligand was reported to form compounds formulated as  $\text{Mn}_2\text{M}(\text{hfac})_6(\text{NIT-pPy})_2$ , where M = Mn, Co, Ni. No crystal structure of these compounds has been reported, although a ladder-like structure has been proposed based on magnetic, far IR, EPR, and X-ray powder diffraction data [5(f)]. All these compounds give rise to spontaneous magnetization below 10 K. Although the interchain connection is accomplished to some extent in these cases, the critical temperature has not increased. NIT-pPy has also been reported to react with lanthanide ion  $\text{Gd}(\text{hfac})_3$  but either isolated molecules or dimer clusters are formed [5(f)].

### 3. METALLIC AND SUPERCONDUCTING POLYMERS

Electrical conductivity of polymers continues to be one of the most important research areas for materials science. The conductivity of metals (typically

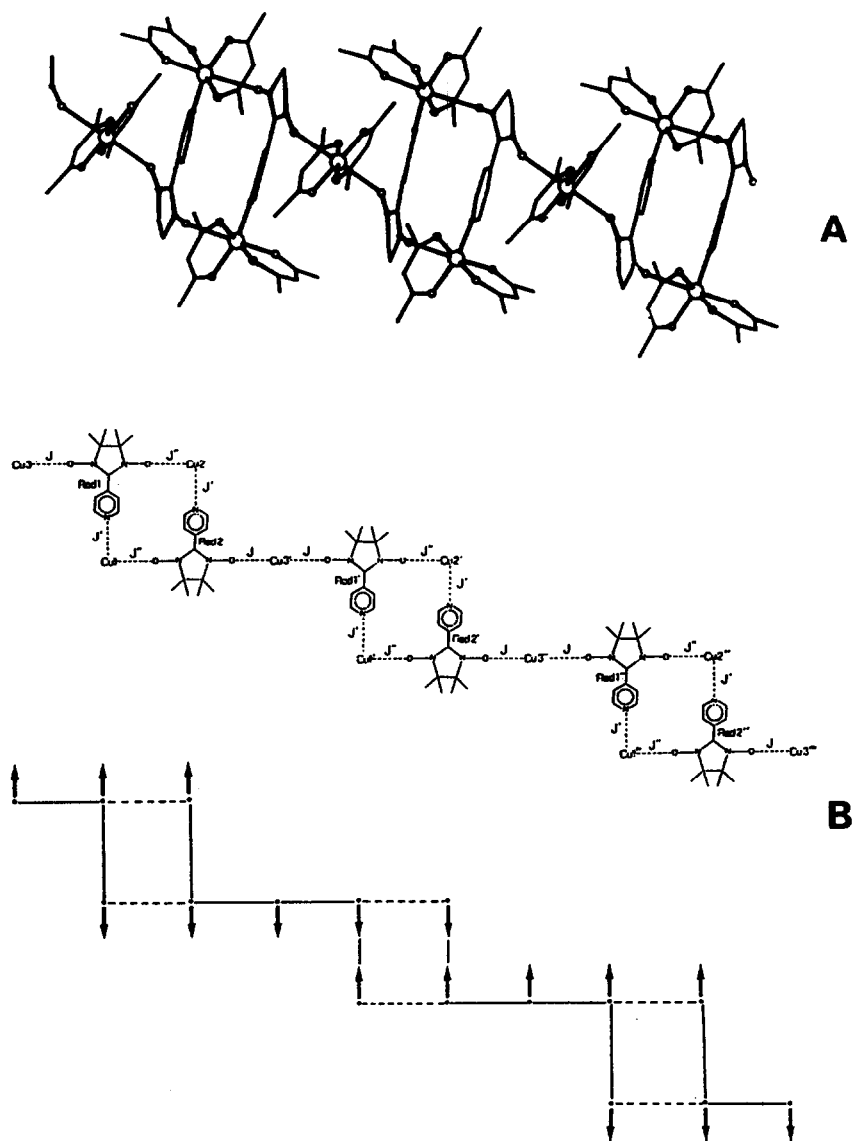


Fig. 4. The chain structure formed by dimeric  $[\text{Cu}(\text{hfac})_2(\text{NIT-pPy})]_2$  unit bridged by  $\text{Cu}(\text{hfac})_2$  moieties. Fluorine atoms and methyl groups are not shown for the sake of clarity. Their spin coupling scheme are also depicted [5(e)].

$10^2 \sim 10^3 \Omega^{-1} \text{ cm}^{-1}$  at room temperature) are generally higher than semiconductors, but it is the temperature dependence that truly defines the difference: electrical conductivity of metallic substances increases with decreasing temperature, while that of a semiconductor decreases [9]. The interest in superconducting materials parallels

the interest in synthetic metals. In a sense, the copper oxide high-temperature superconductors (e.g.  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with  $T_c \sim 95$  K) are two-dimensional coordination polymers, but we will not discuss them further here [10].

Another class of synthetic metals is based on  $\pi$ -conjugated organic molecules which form one-dimensional stacks or two-dimensional sheet structures [11]. TTF-TCNQ (TTF = tetrathiofulvalene, TCNQ = tetracyanoquinodimethane) was the first organic solid with metallic conductive behavior. This class of molecular-based conductors possesses an important structural feature: segregated, double one-dimensional stacks with partial charge-transfer between stacks. This has become a common model for most other synthetic organic conductors [12]. In a few cases, coordination polymers of anions promote the superconductivity of these materials. For example, in  $\beta$ -(ET) $_2$ X (where ET = bis(ethylenedithio)tetrathiafulvalene; X =  $\text{IBr}_2^-$ ,  $\text{AuI}_2^-$  and  $\text{I}_3^-$ ), the longer the anions, the higher the superconducting transition temperature [13];  $T_c = 2.8, 5,$  and  $8$  K for X =  $\text{IBr}_2^-$ ,  $\text{AuI}_2^-$  and  $\text{I}_3^-$ , respectively [14]. This suggests that, if the anions form a polymeric sheet-like 2D structure, the anticipated donor radical network is expected to be layer-like, similar to the proven organic superconductors [14]. There are several ambient pressure superconductors based on ET radical donor and polymeric anions with higher  $T_c$ , e.g.  $\kappa$ -(ET) $_2\text{Cu}(\text{NCS})_2$  ( $T_c = 10.4$  K) and  $\kappa$ -(ET) $_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br}$  ( $T_c = 12.5$  K). The crystal structure of both compounds has alternating layers of ET donor molecules and polymeric anions,  $[(\text{SCN})\text{Cu}(\text{NCS})]_\infty$  and  $\{[\text{Cu}(\text{N}(\text{CN})_2)\text{Br}]_\infty$ , respectively (Fig. 5(b),(c)) [15]. All S–S intermolecular contacts within a dimer are longer than the sum of the van der Waals radius (3.6 Å), but shorter contacts occur between dimers, i.e. this is not a one-dimensional columnar stack, but rather a two-dimensional network structure (Fig. 5(a)) [16].

Another type of one-dimensional coordination polymer conductors has direct overlap of  $d_{z^2}$  orbital of metal atoms. Best known are the cyanoplatinum salts,  $[\text{Pt}(\text{CN})_4]^{n-}$ , and halocarbonyliridium salts,  $[\text{Ir}(\text{CO})_2\text{Cl}_2]^{n-}$ . They both are cation-deficient salts (with  $n < 1$ ) and have metal–metal distances shorter than 2.9 Å. The room-temperature conductivity can be as high as  $2300 \Omega^{-1} \text{cm}^{-1}$  for  $\text{Rb}_2[\text{Pt}(\text{CN})_4](\text{FHF})_{0.4}$  (Fig. 6(a)) [17] and  $5.0 \Omega^{-1} \text{cm}^{-1}$  for  $\text{K}_{0.58}[\text{Ir}(\text{CO})_2\text{Cl}_2]$  [18]. On the other hand, dioxalatoplatinum salts  $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{n-}$  have a similar structure to those of cyanoplatinum salts (Fig. 6(b)) [19], but are only semiconductors, e.g.  $\sigma_{300\text{K}} = 7 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$  for  $\text{Rb}_{1.67}[\text{Pt}(\text{C}_2\text{O}_4)_2]$ . It was shown that the semiconductor behavior of dioxalatoplatinum salts is due to the periodical variation of the charge density along the Pt chains (with variable Pt–Pt bond distances from 2.7 to 3.0 Å).

A large number of planar metal complexes also form one-dimensional stacked structures [11]. These are usually complexes of Ni, Pd, or Pt with flat  $\pi$ -conjugated ligands (Fig. 7). Although there is a variety of possible spatial arrangements for the one-dimensional stacking structures (Fig. 8), they all suffer Peierls instability, and none are superconductors even at low temperatures. (The Peierls instability or



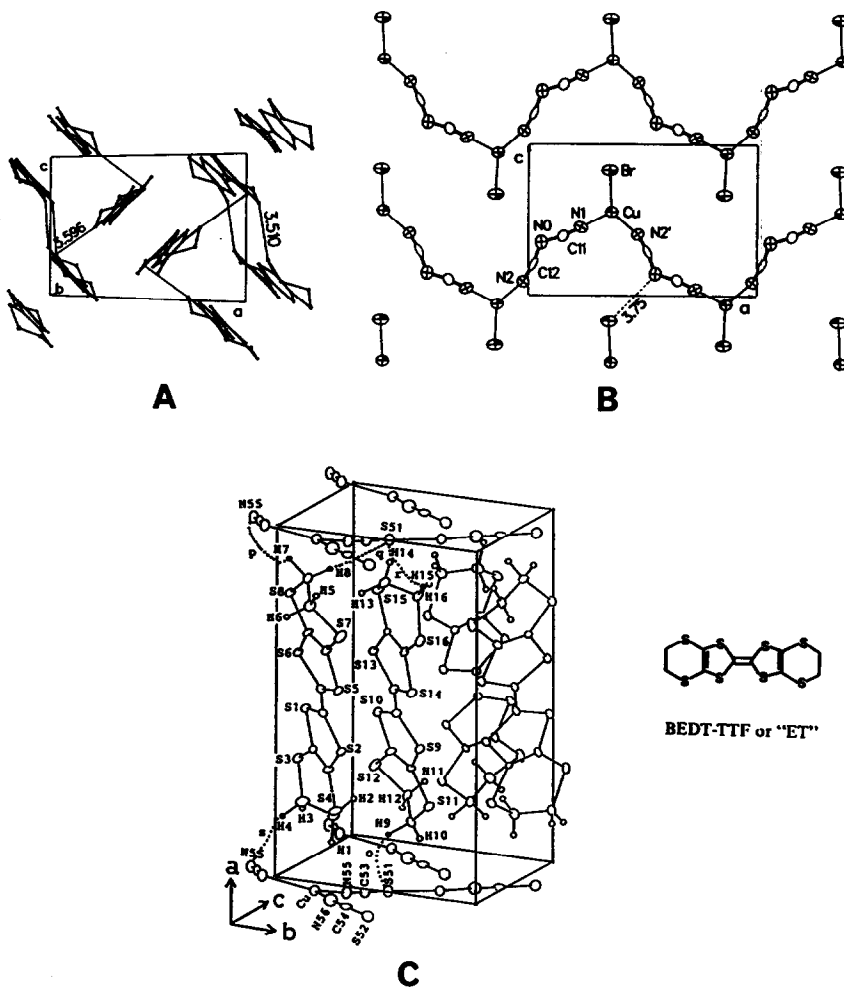


Fig. 5. Crystal Structures of (A) the ET donor layer in  $\kappa$ -(ET) $_2$ Cu[N(CN) $_2$ ]Br, (B) polymeric anion layer of  $\kappa$ -(ET) $_2$ Cu[N(CN) $_2$ ]Br, and (C)  $\kappa$ -(ET) $_2$ Cu(NCS) $_2$ . Note the polymeric anion layers sandwich the ET layer in (C) [15].

distortion is a solid state phenomenon analogous to Jahn–Teller distortions in mononuclear complexes, i.e. a structural distortion that lowers the energy of the system by breaking symmetry [12(b)]. These metal complexes often stack with a separation distance around 3.4 Å, which is the optimal distance for  $\pi$ – $\pi$  interactions, but far too long for direct interaction between metal atoms (e.g. 2.8 Å for the Pt–Pt single bond). Most of these insulators or semi-conductors can be promoted to conductors after the partial oxidation. With few exceptions, however, such materials undergo a low-temperature transition with loss of conductivity.

Ni(Pc)(I $_3$ ) $_{0.33}$ , where Pc = the dianion of phthalocyanine [11(f)], is particularly



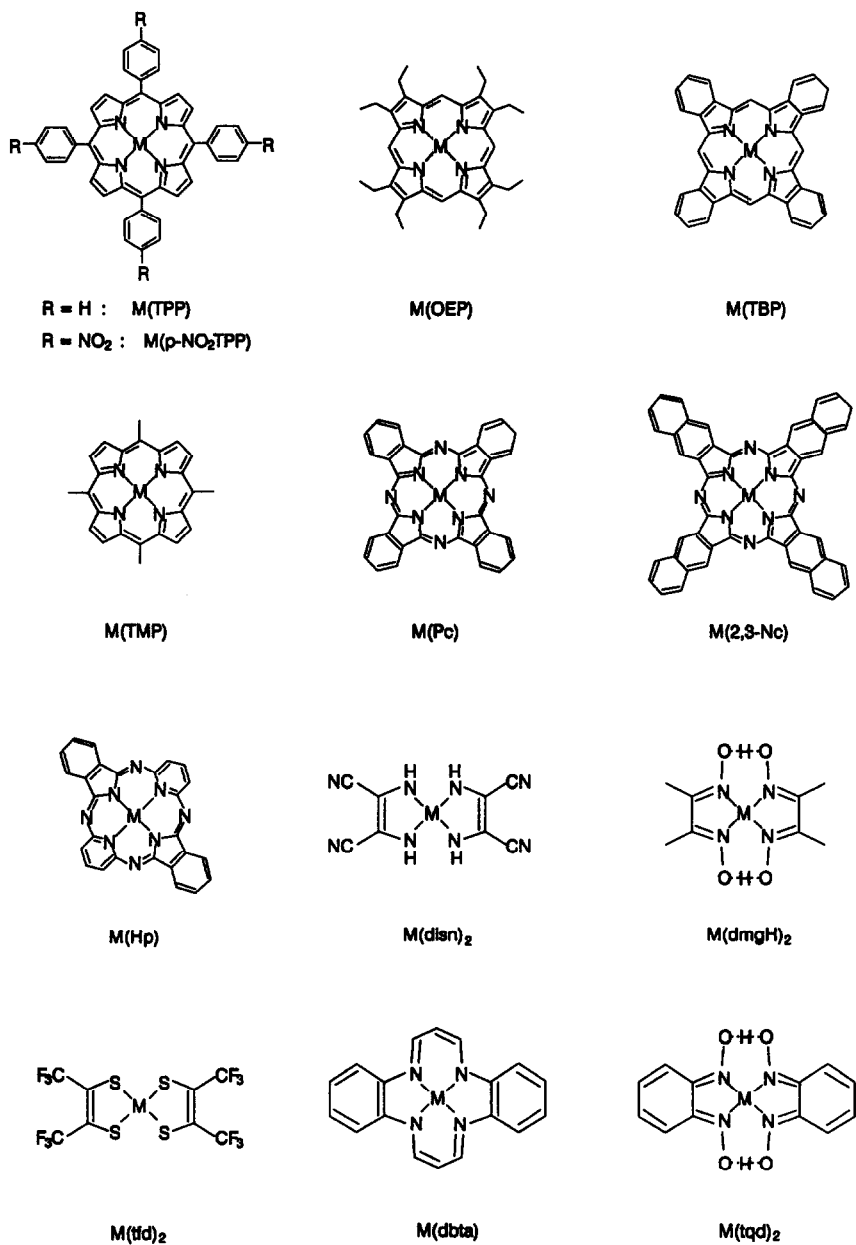


Fig. 7. Various metallocyclic complexes suitable for one-dimensional stacking structures.

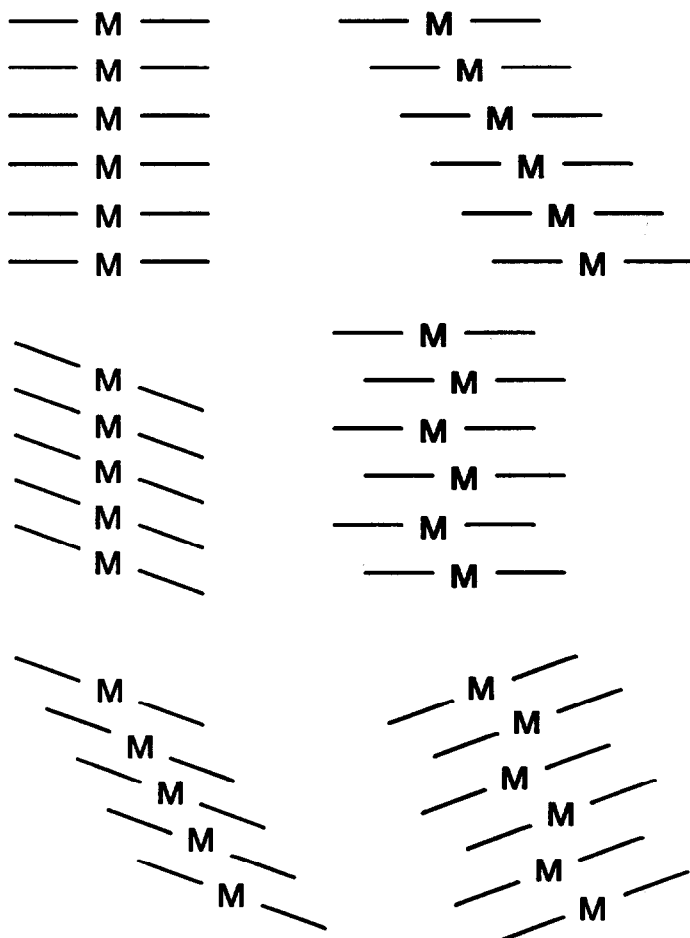


Fig. 8. One-dimensional stacked metal complexes with a variety spatial arrangements.

Phthalocyanine complexes have been intensely studied as coordination polymers. Its polysiloxane polymers  $[M(\text{Pc})\text{X}]_{\infty}$  ( $M = \text{Si, Ge, Sn; X} = \text{O}$ ) were first synthesized in the early 1960s by Joyner and Kenney from the dehydration of dihydro derivatives  $M(\text{Pc})(\text{OH})_2$  in vacuo [20]. Similar polymeric structures with  $M = \text{Al, Ga, Cr; X} = \text{F}$  have also been reported [21]. The structure of these single-atom bridged polymers was not verified until the X-ray single-crystal structure of the fluoro-bridged gallium phthalocyanine  $[\text{Ga}(\text{Pc})\text{F}]_{\infty}$  was obtained in 1982 [21(c),(d)]. The conductivity of these polymers was heavily studied by both Kenney and co-workers [21] and Marks and co-workers [22(a),(b),23,24]. These single-atom bridged polymers, doped by halogens or other inorganic [22] or organic acceptors [23], result in dramatic enhancements in electrical conductivity as well as in the appearance of the characteristic magnetic and optical signatures of a “molecular metal”. The

crystal structure of the oxo-bridged iron complex polymer  $[\text{Fe}(\text{Hp})\text{O}]_{\infty}$  (Hp = the dianion of hemiporphyrizine) was also reported [25], although doping does not lead to an increase in conductivity.

The “shish kebab” approach [26(h),27(a)] yields another class of coordination polymer of stacked macrocyclic metal complexes (Fig. 9). Here, macrocyclic complexes are linked together by axial coordination of bridging ligands. Until recently, “shish kebab” polymers with bridging ligands larger than a single atom were rare.  $[\text{Sn}^{\text{IV}}(\text{OEP})(\text{pim})]_{\infty}$  (OEP = octaethylporphyrinate; pim = dianion of pimelic acid) and  $[\text{Zr}(\text{OEP})(\text{suc})]_{\infty}$  (suc = the dianion of succinic acid) were two early examples [28]. In the late 1970s, Hanack et al. started to prepare a large family of such polymers employing phthalocyanines of the type  $[\text{M}(\text{Pc})(\text{L}-\text{L})]_{\infty}$  (Fig. 9) [26].

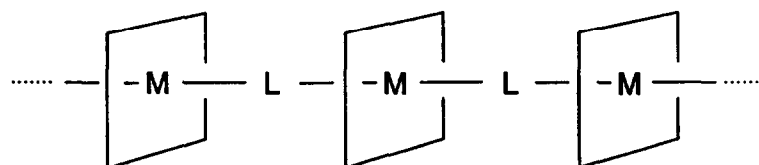
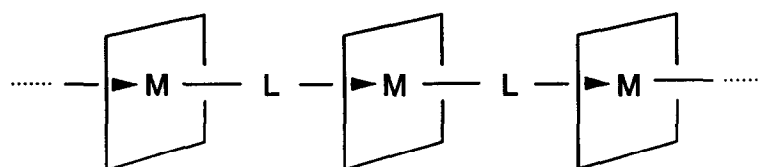
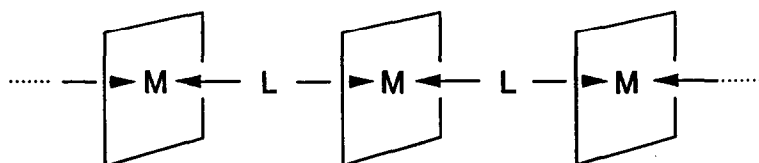


Fig. 9. Various “shish kebab” one-dimensional coordination polymers.

Recently, Collman et al. reported similar “shish kebab” polymers of the type  $[M(OEP)(L-L)]_{\infty}$  ( $M = Fe, Ru, Os$ , and  $L-L = pyz, bpy, dabco$ ) and examined their conductivities [27]. Many of these “shish kebab” coordination polymers can be doped with iodine, [26(h),(j)], which drastically increases their conductivity (e.g.  $\sigma_{300K} = 1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$  for  $[Fe^{II}(Pc)(pyz)]_{\infty}$ ;  $\sigma_{300K} = 2 \times 10^{-1} \Omega^{-1} \text{cm}^{-1}$  for  $[Fe^{II}(Pc)(pyz)I_{2.54}]_{\infty}$ ). The conductivity of these doped “shish kebab” polymers depends on the interaction of metal’s  $d_{\pi}$  orbitals with the  $\pi^*$  level of the bridging ligand. Collman et al. [27] found that the metal–metal communication is greater for the better  $\pi$ -bonding metals (e.g.  $Os > Ru > Fe$ ) and the more  $\pi$ -acidic bridging ligand (e.g.  $pyz > bpy \gg dabco$ ). The X-ray single-crystal structure of the related non-macrocyclic metal complex  $[Co^{II}(dmgH)_2(pyzy)]_{\infty}$  confirms that the polymeric “shish kebab” type structure can be formed with symmetric multiatom bridges [29].

#### 4. NON-LINEAR OPTICAL (NLO) MATERIALS

Enormous efforts are being made in the development of NLO materials for their use in frequency conversion and intensity modulation [30]. There are two common classes of NLO materials: inorganic metal oxides or phosphates with distorted metal oxygen octahedral structures (e.g.  $LiNbO_3, KTiOPO_4, KH_2PO_4$ ) and organic molecular solids composed of donor–acceptor substituted aromatic molecules (e.g. 2-methyl-4-nitroaniline and 3-methyl-4-nitropyridine-*N*-oxide) [31]. More recently, poled organic polymer films containing NLO organic molecule are finding potential applications in the fabrication of integrated electro-optical circuits [32]. There are, however, only a few cases of one-dimensional coordination polymers studied for their NLO properties.

The best known NLO one-dimensional coordination polymer is potassium titanyl phosphate,  $KTiOPO_4$ , also known as KTP. KTP is one of the most promising non-linear optical materials [31(e),33(b)]. The high non-linear optical coefficient, high optical damage threshold, low threshold power, and low phase-matching sensitivity make KTP a better material than either  $KH_2PO_4$  or  $LiNbO_3$ , which are the current workhorses for second harmonic generation (SHG) of the 1.064- $\mu\text{m}$  YAG laser [31]. KTP can also be viewed as a cross-linked coordination polymer. KTP crystallizes in a non-centrosymmetric space group ( $Pna2_1$ ), which is a necessary condition for a non-zero second order NLO susceptibility. The crystal structure of KTP is composed of distorted  $TiO_6$  octahedrons, which are linked to each other through shared corner oxygen atoms to form zigzag chains parallel to [001] (Fig. 10) [31(e),33(a)]. Phosphate units cross-link the neighboring chains to form the three-dimensional network structure of KTP. For each distorted octahedron around the titanium atom, there is a short ( $<1.75 \text{ \AA}$ ) Ti–O bond trans to a long ( $>2.10 \text{ \AA}$ ) Ti–O bond. Stucky et al. demonstrated that selective deammoniation of the ammonium analogue of KTP,  $(NH_4)_2(TiOPO_4)_2$ , to  $(NH_4)(H)(TiOPO_4)_2$  reduced the bond length alternation of O–Ti–O and also diminished the SHG signal [31(e),34]. The asymmetric O–Ti–O

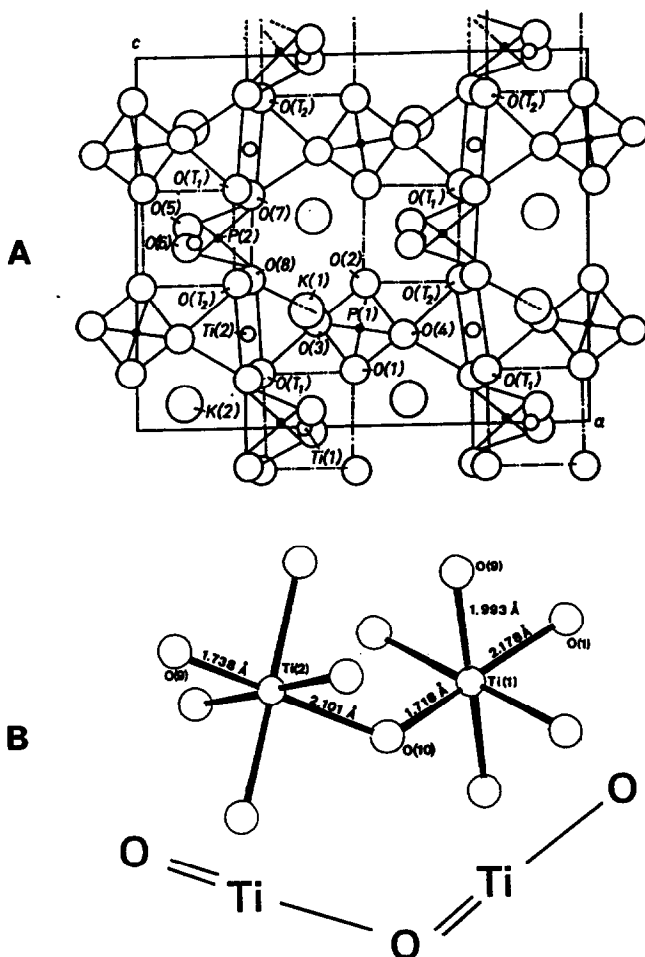


Fig. 10. Crystal structures of  $\text{KTiOPO}_4$ : (A) view of the unit cell along the  $[010]$  direction, (B) Ti coordination environment in asymmetric unit indicating  $\text{O}=\text{Ti}-\text{O}$  bond alternation pattern [31(e),33(a)].

bonding structures along the  $\text{TiO}_6$  chain act as the polarization centers which are primarily responsible for the microscopic second-order susceptibility ( $\beta$ ) of KTP. The similar bond-length alternations are also found in the inorganic NLO material  $\text{LiNbO}_3$  [33(c)–(f)].

Several other one-dimensional coordination polymers have been recently examined for their SHG properties. Like KTP, these coordination polymers all crystallize in non-centrosymmetric lattices.  $\text{Mn}(\text{hfac})_2(\text{NIT-R})$ , with  $\text{R} = 4$ -methoxyphenyl, is one of the molecular ferromagnets based on NIT-R radical nitronyl oxides. Due to the bulky substituent, two hfac ligands are coordinated to the Mn atom in the cis position (Fig. 11(a)) [35]. Thus, each  $\text{Mn}(\text{hfac})_2$  moiety is linked to form an acentric helix one-dimensional polymeric structure (Fig. 11(b)). The metal complexes,

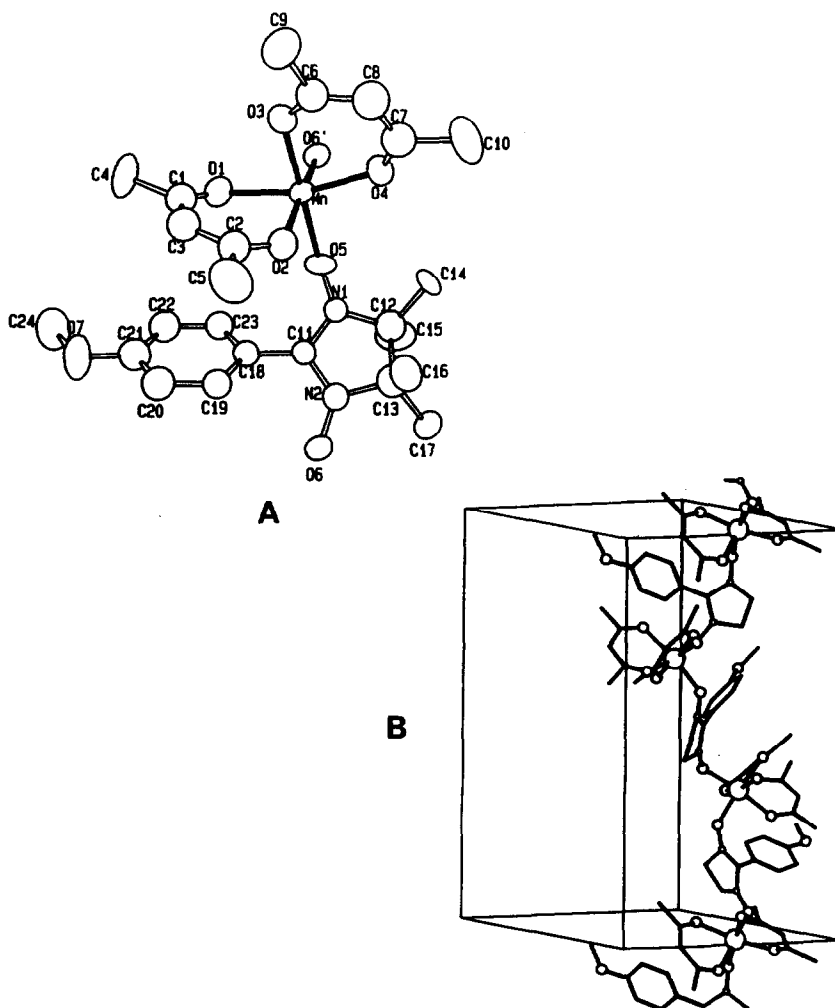


Fig. 11. Crystal structures of  $[\text{Mn}(\text{hfac})_2(\text{NIT-PhOMe})]_\infty$ . (A) The asymmetric unit of the molecule with fluorine atoms omitted. Note that the two hfac molecules are in cis position. (B) Simplified view of the polymeric helix chain on the unit cell [35].

$\text{Mn}(\text{hfac})_2$ , provide a suitable acentric framework to keep the radical properly oriented in the lattice. A sizable SHG signal from a Nd-YAG laser ( $\lambda = 1064 \text{ nm}$ ) has been detected from the powdered sample. It has been suggested that the NLO properties is associated with the radical of such compound.

Metal-nitrido complexes have also been known to form polymeric chain structures (Fig. 12) [36]. The polymeric chains consist of alternating short ( $< 1.7 \text{ \AA}$ ) and long ( $> 2.6 \text{ \AA}$ ) M–N bonds, corresponding formally to triple and weak dative single bonds, respectively. The alternating bond system  $-\text{N}-\text{M}\equiv\text{N}-$  can be regarded as an



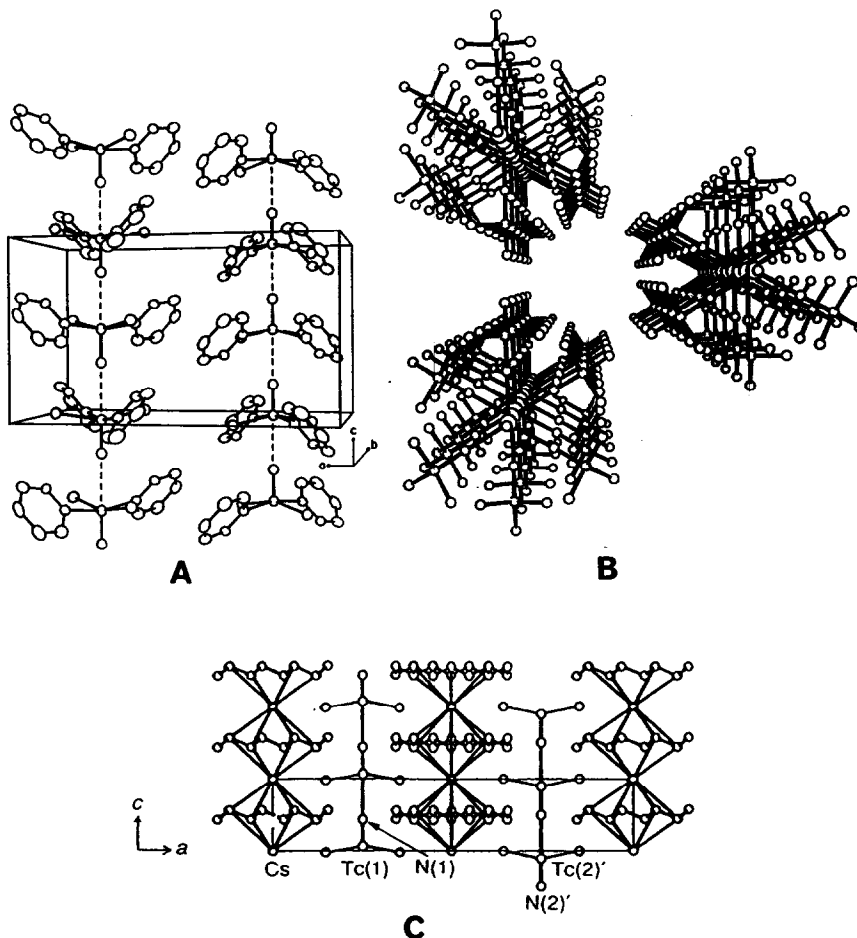


Fig. 12. Crystal structures of some one-dimensional coordination polymers with metal–nitrido bonds: (A)  $[V(\mu-N)Cl_2(py)_2]_\infty$ , (B)  $[W(\mu-N)(O-t-Bu)]_\infty$ , (C)  $\{Cs(18-c-6)\}[Tc(\mu-N)Cl_4]_\infty$  [36].

inorganic analog of hydrocarbon polyenes and polyynes whose NLO properties have been extensively studied.  $[W(\mu-N)(OCMe_3)_3]_\infty$  and  $[W(\mu-N)(OCMe_3)_3]_\infty$ , which crystallize in non-centric space groups ( $P6_3cm$ ,  $P6_3$ ), have been examined for their SHG response on powdered samples [37]. Their SHG efficiency, however, was low compared with urea ( $\sim 0.3$ ). It was shown that the electrons are not extensively delocalized along the polymer chain because of the long dative M–N bonds.

Thompson and co-workers synthesized one-dimensional coordination polymers of  $M(\text{SALEN})(X)$  where  $M = \text{Cr, Mn, Fe, and Co}$  and  $X = \text{NCCH}_2^-, \text{NC}_5\text{H}_4\text{NHCH}_2\text{CO}_2^-, \text{and } \text{NC}_5\text{H}_4\text{NHCH}_2\text{SO}_3^-$  (Fig. 13(a)) [38].  $M(\text{SALEN})(X)$  complexes form dipolar coordination polymer in the solid-state because of the bridging ligands. The bridging ligands have donor and acceptor substituents and align in a

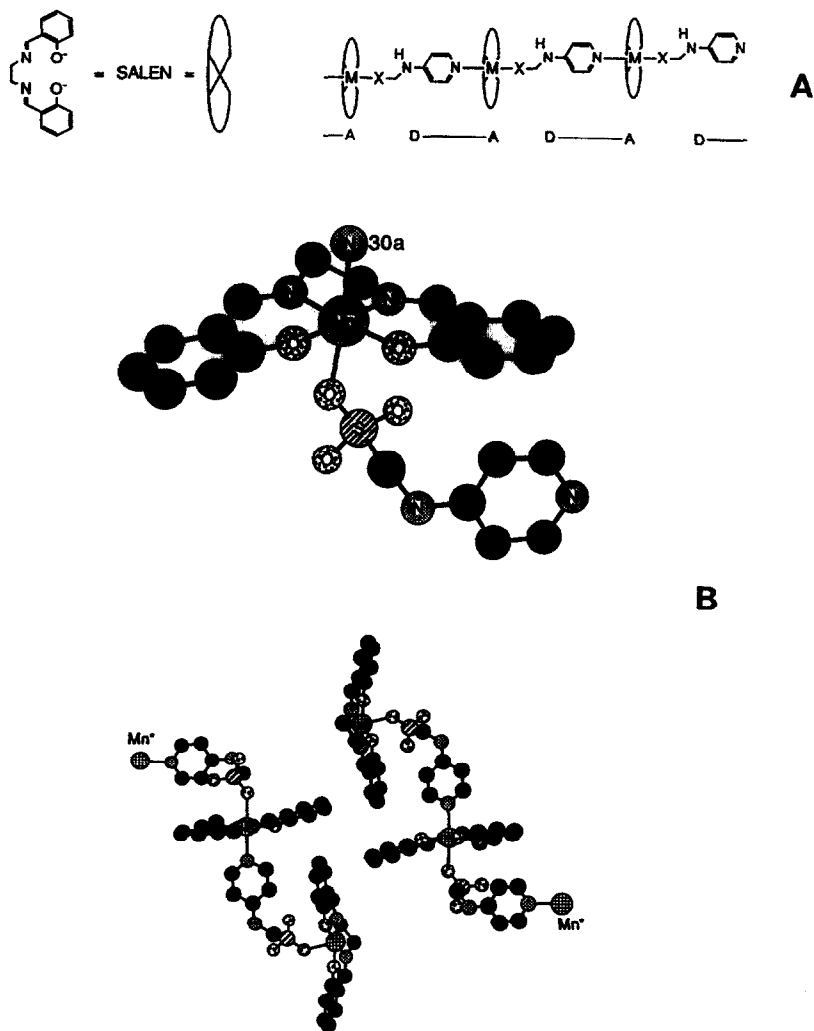


Fig. 13. (A) Structure of SALEN and dipolar coordination polymers (where D and A denote the donor and acceptor, respectively;  $X = \text{CO}_2^-$  and  $\text{SO}_3^-$ ). (B) Crystal structure of  $[\text{Mn}(\text{SALEN})(\text{O}_3\text{SCH}_2\text{NHC}_5\text{H}_5\text{N})]_\infty$  [38(a)].

head-to-tail direction, forming a polar polymer chain in the solid state, as shown in the crystal structure of  $[\text{Mn}(\text{SALEN})(\text{O}_3\text{SCH}_2\text{NHC}_5\text{H}_5\text{N})]_\infty$  (Fig. 13). Due to the non-linear geometry of  $\text{RCO}_2^-$  and  $\text{RSO}_3^-$ , the chains propagate in a zigzag fashion, resulting in an almost perpendicular orientation of the adjacent SALEN rings. The intramolecular charge-transfers (ICT) of these polymers originate from both the M(SALEN) center (MLCT or LMCT) and the donor–acceptor substituted bridging ligands. The conformation of the zigzag polymer chain results in a partial cancellation of the overall polarization, thus reducing the SHG efficiencies of these polymers.

Furthermore, these polymers tend to pack with an antiparallel arrangement, which makes them ineffective for second-order NLO properties. After recrystallization from triethylamine/methanol, the same compounds showed low but measurable SHG efficiencies (less than 20% of that of urea at 1907 nm on powder samples).

Soluble rigid-rod polyyne polymers  $trans\text{-}\{(\text{Pt}[\text{P}(n\text{-Bu})_3]_2)(\text{-C}\equiv\text{C-X-C}\equiv\text{C-})\}_n$ , originally prepared by the Hagihara group [39], have been shown to exhibit large third-order optical non-linearities,  $\gamma = 1200\text{--}4400 \times 10^{-36}$  esu, which are comparable with the  $\gamma$  values of inorganic semiconductors such as Ge ( $2300 \times 10^{-36}$  esu) [40]. The third-order non-linearity of Ge is among the highest reported non-resonance values [33(b)]. Unlike Ge, however, the platinum polyyne polymers are transparent in the visible wavelengths. It was found that the  $\gamma$  values of these polymers increase with increasing length of the organic portion of the polymer repeat units as well as with the increasing chain length of the polymers [40]. Marder and co-workers [41] prepared a similar rhodium derivative with general form  $mer\text{-}trans\text{-}[\text{Rh}(\text{PR}_3)_3(\text{H})(\text{-C}\equiv\text{C-X-C}\equiv\text{C-})]_n$ . They suggest that larger third-order optical non-linearities will result from improved conjugation along the polymer chain. Since the conjugation is a result of  $\pi$ -backbonding from filled metal d-orbitals into empty acetylide  $\pi^*$ -orbitals, raising the energies of the metal d-levels or lowering the energies

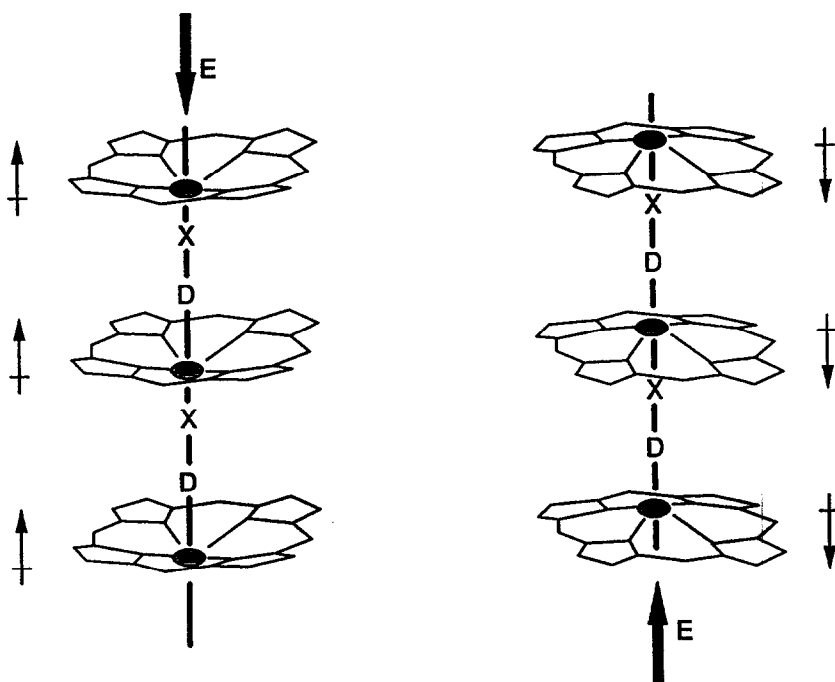


Fig. 14. Schematic representation of a ferroelectric coordination polymer and dipole moment switching in response to an external field [44(b)].

of the acetylide  $\pi^*$ -levels will enhance these interactions. The use of transition metals to the left of platinum and increasing numbers of donor ligands (e.g. 3 or 4, rather than 2) raises metal d-orbital energies.

#### 5. FERROELECTRIC MATERIALS

Very little work has been done on the development of coordination polymers as molecular-based ferroelectric materials. Ferroelectrics carry a permanent, macroscopic electric dipole moment (i.e. polarization) in the absence of electric field. Furthermore, the polarization of ferroelectric materials can be switched with the application of an external electric field. Ferroelectrics have unusual electro-optical, photorefractive and pyroelectric properties. They can be fabricated into electronic oscillators, high-frequency filters, electroacoustic converters, pyroelectric radiant-energy receivers, and non-linear capacitive elements. Most ferroelectrics are metal oxides [42] (such as  $\text{BaTiO}_3$  and  $\text{LiNbO}_3$ ); a few are liquid-crystal materials [43].

In a further development of the “shish kebab” class of polymer, metalloporphyrin coordination polymers have been suggested as possible ferroelectric materials [44]. Coordination polymers of non-planar metalloporphyrins with *non-symmetrical* bridging ligands carry a net and aligned dipole moment along the stacking axis

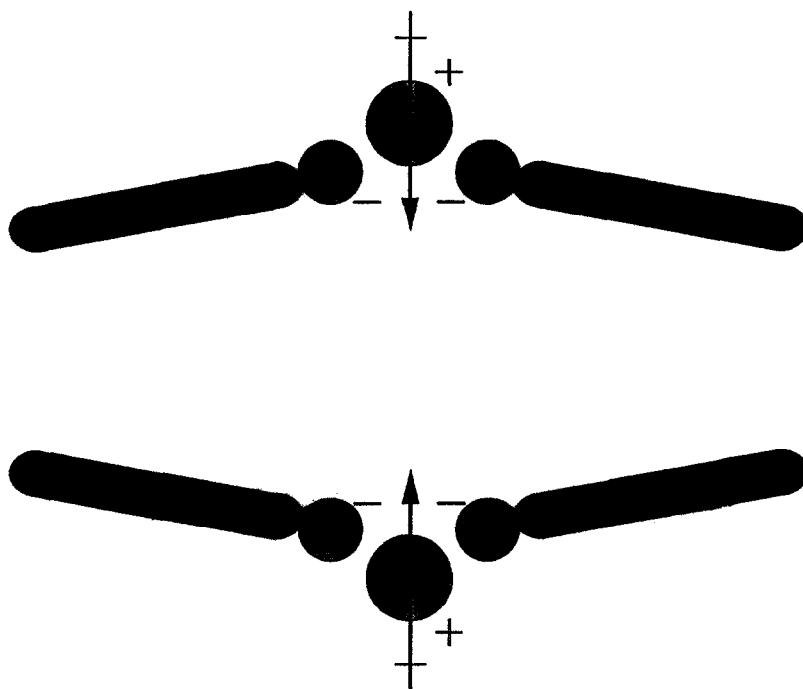


Fig. 15. The dipole moment of metalloporphyrins [44(b)].

(Fig. 14). The dipole moment originates from the charge separation between the bowl-shaped porphyrinato core and the metal atom (Fig. 15). Metal atoms tend to be pulled out of the porphyrin plane by a stronger axial ligand. If the metalloporphyrin has two different axial ligands, the metal atom will be pulled toward one side or the other, depending on relative ligation strength and steric demands. Various monomeric structures of metalloporphyrins [45–48] suggest that a double-well potential can be present, as shown schematically in Fig. 16. By analogy to the metal oxide compounds [49], the direction of the bulk polarization in such coordination polymers may respond to an external field.

Suslick and Chen have prepared several one-dimensional coordination polymers of metalloporphyrins with non-symmetric bridging ligands (Fig. 17) as candidates for molecular ferroelectric materials [44]. Metalloporphyrin complexes of Fe(II), Fe(III) and Sn(IV) were examined. The single-crystal X-ray structures determined included  $[\text{Fe}^{\text{II}}(\text{TPP})(\text{pyCN})]_{\infty}$ ,  $[\text{Fe}^{\text{III}}(\text{TPP})(\text{pyCO}_2)]_{\infty}$ , and  $[\text{Fe}^{\text{III}}(\text{TPP})(\text{ImPhO})]_{\infty}$  (Fig. 18). The chain alignment of the bridging ligand is disor-

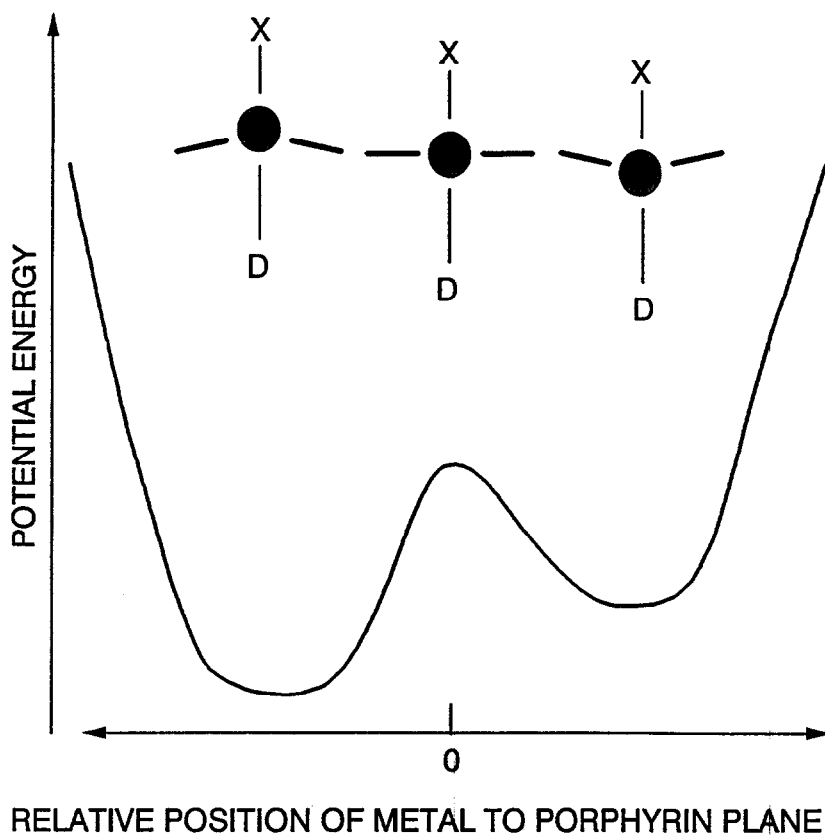


Fig. 16. The double-well potential of the position of the metal atom relative to the porphyrin core [44(b)].

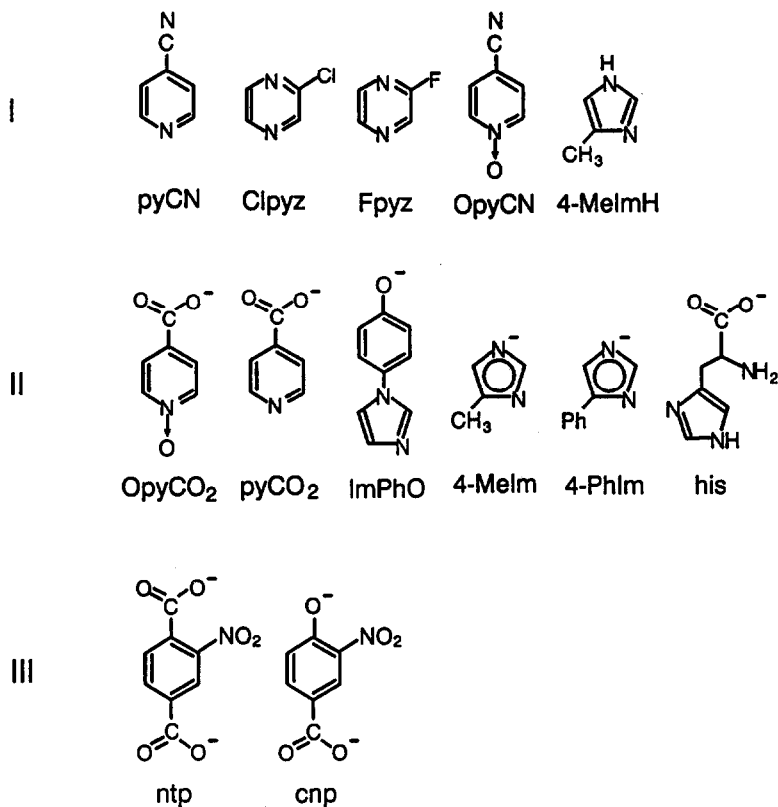


Fig. 17. Three classes of the non-symmetrical bridging ligands [44(b)].

dered in  $[\text{Fe}^{\text{II}}(\text{TPP})(\text{pyCN})]_{\infty}$ , antiparallel in  $[\text{Fe}^{\text{III}}(\text{TPP})(\text{pyCO}_2)]_{\infty}$ , but aligned and polar in  $[\text{Fe}^{\text{III}}(\text{TPP})(\text{ImPhO})]_{\infty}$ .  $[\text{Fe}^{\text{III}}(\text{TPP})(\text{ImPhO})]_{\infty}$  crystallizes in a non-centrosymmetric space group,  $Pna2_1$ , and the normal to the metalloporphyrin ring is about  $20^\circ$  off the  $c$  axis. Therefore, a net dipole moment or macroscopic polarization parallel to the  $c$  axis can be expected only from  $[\text{Fe}^{\text{III}}(\text{TPP})(\text{ImPhO})]_{\infty}$ . The small size of the doming of the porphyrin in this complex, combined with the large unit cell dimensions, suggests that the spontaneous polarization of  $[\text{Fe}^{\text{III}}(\text{TPP})(\text{ImPhO})]_{\infty}$  will be much smaller than that of  $\text{BaTiO}_3$  [50]. The organic part of the  $\text{Fe}^{\text{III}}(\text{TPP})(\text{ImPhO})$  polymer does not contribute much to the dipole moment, although it is the major component in the unit cell.

Similar stacking structures without the bridging ligand formed by bowl-shaped or cone-shaped molecules have been reported for lead phthalocyanine  $\text{Pb}(\text{Pc})$ , metacyclophanes, and cyclotricatechylenes. The crystal structures of some of these have been reported [51]. These molecules are capable of columnar stacking along the dipolar axis of the molecules. The dipole moment of each unit in such stacks can be quite high [51(i)]. Because of the high dipole moment of these conical molecules,

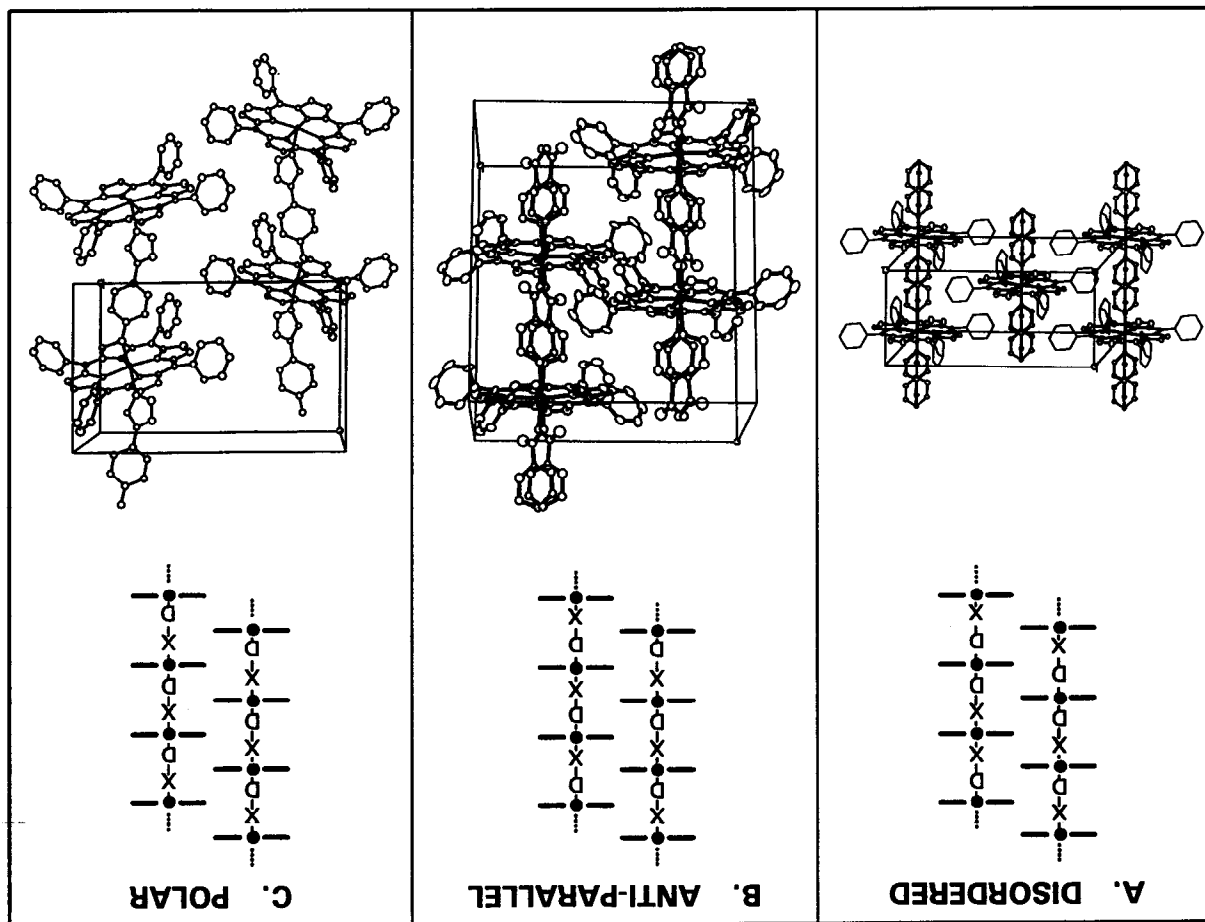


Fig. 18. Three alignments of bridging ligands in metalloporphyrin coordination polymers and ORTEP plots of the packing diagrams. (A)  $[\text{Fe}^{\text{II}}(\text{TPP})(\text{pyCN}) \cdot 2\text{C}_6\text{H}_6]_{\infty}$ , solid and hollow bonds drawn for bridging ligands and two phenyl rings represent the disordered structures. (B)  $\text{Fe}^{\text{III}}(\text{TPP})(\text{pyCO}_2) \cdot \text{C}_7\text{H}_8_{\infty}$ . (C)  $[\text{Fe}^{\text{III}}(\text{TPP})(\text{ImPhO})]_{\infty}$ . For clarity, solvent molecules and hydrogen atoms are omitted and only two of the four polymeric chains in the unit cell are shown in (C). Two sets of pyCN in (A) and of pyCO<sub>2</sub> in (B) are shown, representing different orientations [44(b)].

however, antiferroelectric columnar or antiparallel dimerized arrangements are usually preferred over the parallel polar stacking required for ferroelectric properties. This tendency towards antiparallel stacking of polar chains has also been noted in macrocyclic coordination polymers [38,44].

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