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# STRUCTURAL AND CONDUCTIVITY ASPECTS OF ONE-DIMENSIONAL TRANSITION METAL COMPLEXES

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CONTENTS

## A. INTRODUCTION

The quest for materials with usual semiconducting and conducting properties has provided impetus for research in the area of "linear chain" or "pseudo-one-dimensional" compounds. These are materials which, by virtue of their crystalline packing arrangements, exhibit anisotropy in certain intensive variables including electrical, optical and magnetic behavior. Three broad categories can be defined for compounds comprising the area of electrical conduction: (1) organic donor-acceptor complexes such as tetrathiofulvalenium-7,7,8,8-tetracyano-*p*-quinodimethanide (TTF-TCNQ); (2) polymeric systems, i.e. polysulfurnitride $(SN)_x$; and (3) transition metal complexes. Square planar coordination complexes, which are included in the third category, have been extensively studied with respect to their unidimensional characteristics. The results indicate that these compounds can be divided into three classes which are the subject of this review.

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Perhaps the most avidly studied anisotropic transition metal complexes are the partially-oxidized, predominantly square-planar, tetracyanoplatinates [1,2]. These are appropriately classified as organometallic compounds due to the presence of metal—carbon $\sigma$ bonds. These materials exhibit anisotropic physical properties, with the most important being the one dimensional (1-D) metallic conductivity along the metal chain axis. Recent investigations have demonstrated that high conductivities and anisotropic properties can also be obtained for complexes of transition metals with larger, more complex macrocyclic ligand systems. In particular, highly planar, organic ligands such as phthalocyanine [3,4] and tetrabenzporphyrin [5] have been shown to form transition metal complexes which are anisotropically conducting materials when oxidized by iodine [3—5]. Other pseudo-macrocyclic systems such as the bis(glyoximates) can also, with certain transition metals, be partially-oxidized by $I_2$ to form complexes with enhanced conductivities as contrasted to their unoxidized forms [6—10]. These compounds, unlike the phthalocyanines, are not strictly planar, particularly in the ligand periphery.

Thus, the cycle of square planar coordinated transition metal complexes ranges from the predominantly planar organometallic, to the strictly planar expanded ligand system organic-metallic, to the non-planar expanded ligand organic-metallic compounds. This review deals mainly with the structural influences on one dimensionality, and the effect of various steric and electronic factors on the formation of highly conducting systems. Aspects such as temperature dependencies and magnetic behavior are not discussed.

## B. DISCUSSION

### (i) General considerations

Several aspects of 1-D and the highly conducting systems should be considered before examining the three classes of transition metal complexes.

#### *Mixed valency*

The electrical properties of a solid are determined to a large extent by its electronic energy levels, their occupation and the gaps between them. According to Band Theory when N atoms are brought together so also are N molecular orbitals covering a range of orbital energies of finite width. At indefinitely large values of N these energies can be considered to form a continuous band for all intents and purposes. Metallic conduction results from the presence of partially-filled bands in which electrons can be readily excited to unfilled orbitals close in energy ($E << kT$) to the highest filled orbital, the result being electron mobility and electrical conduction. The presence of non-integral oxidation states and hence the creation of partially-filled bands thus becomes an important factor in the creation of highly conducting systems. The theory behind charge transport has been treated in detail elsewhere [11—

13]. Briefly, in systems with integral oxidation states charge is mobilized through the creation of states in which positive and negative ions are separated along the chain, while partially-oxidized systems already have holes which have been formed as a result of fractional oxidation. In order for the former to occur, a large activation energy is required. In the latter, however, charge transport can readily occur by movement of the holes between degenerate configurations.

### *Steric aspects*

For strong intermolecular interactions to occur, close molecular approach is a necessity. One way to facilitate this is accomplished by square planar coordination about the metal ion, and by using planar ligand systems. (In the transition metal area efforts to achieve 1-D chains by using binuclear complexes $M_2L_6$ or $M_2L_4$ have not been as successful.) Short metal—metal distances that are only 0.1 to 0.3 Å longer than those in the parent metal have been obtained in the partially-oxidized square planar tetracyanoplatinates by premeditated design [14]. Even for organic molecular metals, a criterion for creating conductive molecular crystals is that the parent compound be a planar complex of metal and ligand [15,16]. The logic behind employing planar systems is evident. Bulky ligands or molecules, while perhaps capable of stacking closely, may not approach each other due to steric repulsions. On the other hand some complexes which show relatively large distortions from planarity have been found to exhibit unexpectedly large conductivities. The partially-oxidized octamethyltetrabenzporphinatonickel(II), Ni(OMTBP)I, is a case in point [16]. In fact, the nickel and palladium bis(diphenylglyoximates), despite the bulky phenyl substituents, display higher conductivities in their partially-oxidized form than the corresponding more planar bis(benzoquinonedioximates). These compounds are discussed in greater detail in section B(iv).

Given that square planar geometry is a desirable characteristic in 1-D transition metal complexes, an investigation into the propensity of various metals for forming this geometry is appropriate. Krogmann has pointed out that metals having accessible $d^8$ electron configuration have a greater tendency to form square-planar coordinated complexes which stack to form columnar structures [1]. Table 1 demonstrates metals with accessible $d^8$ electron configurations. Presently only Pt, Ir and Rh (in decreasing order of occurrence) have been observed to form 1-D metal chain structures with extremely short metal—metal separations. The compounds formed from zero valent states of Fe, Ru, and Os favor trigonal bipyramidal geometries or clusters which tends to prevent chain formation and hence extended metal—metal interactions.

### *Electronic considerations*

Electronic considerations are also of major importance as can be seen by examining the capacity of the $d^8$ metals for forming highly conducting 1-D systems. If, as is often the case in transition metal complexes, the intermolecu-

TABLE 1

Metals with accessible $d^8$ electron configurations

| Configuration | Metal (oxidation state) | | | |
|---|---|---|---|---|
| $3d^8$ | Fe(0) | Co(+1) | Ni(+2) | Cu(+3) |
| $4d^8$ | Ru(0) | Rh(+1) | Pd(+2) | Ag(+3) |
| $5d^8$ | Os(0) | Ir(+1) | Pt(+2) | Au(+3) |

lar interaction involves overlapping *d* orbitals, orbital spatial extension is a major consideration. Due to $5d > 4d > 3d$ orbital extension the most highly conducting complexes would be expected for third row transition metals. Thus both $Pt^{2+}$ and $Ir^{1+}$ form complexes which exhibit metallic conduction, but $Au^{3+}$ does not, due to a contracted 5*d* orbital as a result of higher effective charge. Accordingly, $Ni^{2+}$ and $Pd^{2+}$ would be expected to form complexes exhibiting lower conductivities. This is observed in 1-D systems where *d* orbital interaction is the major contributing mechanism of conduction. For organic moieties where $P_Z$ orbital interactions become important, a similar reasoning would suggest that the heavier Group IV elements such as Si would be a better choice in synthesizing organic 1-D compounds, all other aspects being equal. The widely differing chemistry of Si and other Group IV elements, compared to C, makes it difficult to prove this assertion, however.

### *Ligand system*

The small, nonbulky ligands which promote a planar configuration and have the correct steric requirements to allow close stacking are limited and mainly involve $CN^-$, CO, and oxalate $(C_2O_4)^{2-}$. $NH_3$ offers steric problems, $S^{2-}$ appears to be too large, and $F^-$ does not combine with transition metals in their low oxidation states. The complexes formed with the expanded ligand systems, while sometimes highly conducting, do not exhibit the close intermolecular spacings readily accessible with the less bulky systems. Even in the more congested, extended ligand systems, as long as steric repulsions are minimized, close intermolecular approach should be allowed by snugly fitting the complexes to each other. In general, however, while intermolecular distances in the partially-oxidized tetracyanoplatinates are of the order of 2.9 Å or even less, the analogous phthalocyanato systems exhibit spacings of 3.2 Å or longer. The mode of conduction, whether via primarily *d*-character orbitals, as in the former, versus ligand-centered conduction in the latter, may also influence the packing of the molecules. Evidently *d* orbital interactions necessitate closer approach, at least on the basis of the experimental evidence cited in the subsequent sections.

The three main classes of transition metal complexes exhibiting square planar coordination and anisotropic behavior are discussed in greater detail below.

### *(ii) Square-planar, organometallic-1-D tetracyanoplatinates*

Oxidation of $Pt(CN)_4^{2-}$ results in the formation of complexes with metallic gold, bronze or copper colors [1,2]. Although a metallic luster does not always signify metallic behavior, in this case the resulting complexes are characterized by anisotropic electrical, magnetic and optical properties. In particular, electrical conductivity along the metal chain and insulating behavior in orthogonal directions are observed. Conductivities along the Pt—Pt chain increase by ca. $10^{10}$ from $5 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ in the unoxidized $K_2Pt(CN)_4 \cdot 3\ H_2O$ to a range of 0.5 to 2100 $\Omega^{-1}\ cm^{-1}$ in the oxidized forms [2,11]. Also in conjunction with oxidation the Pt—Pt distances along the chain decrease from 3.478 Å in $K_2Pt(CN)_4 \cdot 3\ H_2O$ to less than 2.95 Å [2,11]. A perspective view of the unit cell of $Rb_2Pt(CN)_4(FHF)_{0.40}$ is illustrated in Fig. 1.

The mechanism of conduction in these complexes is metal centered involving electron delocalization along overlapping $d_z{}^2$ orbitals of the platinum. Partial oxidation is achieved by inclusion of small amounts of anion (e.g. $Br^-$, $Cl^-$, $F^-$, $HF_2^-$, $Br^-Cl^-$, $O_3SOHOSO_3^{3-}$, $N_3^-$, $ClO_4^-$) or by making the cation deficient [17]. ($K^+$, $Rb^+$, $Cs^+$, $NH_4^+$, and guanidinium are typical cations.) The anion deficient tetracyanoplatinates display somewhat higher conductivities than the cation deficient types. Among the anion deficient salts two structural types exist (primitive and body centered lattices). The hydrated salts form the primitive tetragonal lattices (*P4mm*) with $M^+$ cations in one-half of the unit cell and water molecules in the other half. The anhydrous salts are body-centered tetragonal (*I4/mcm*) and the cations occupy sites in the same plane as the $Pt(CN)_4^{2-}$ groups. The tendency toward hydration in the Krogmann salts is found to depend on both cation and anion.

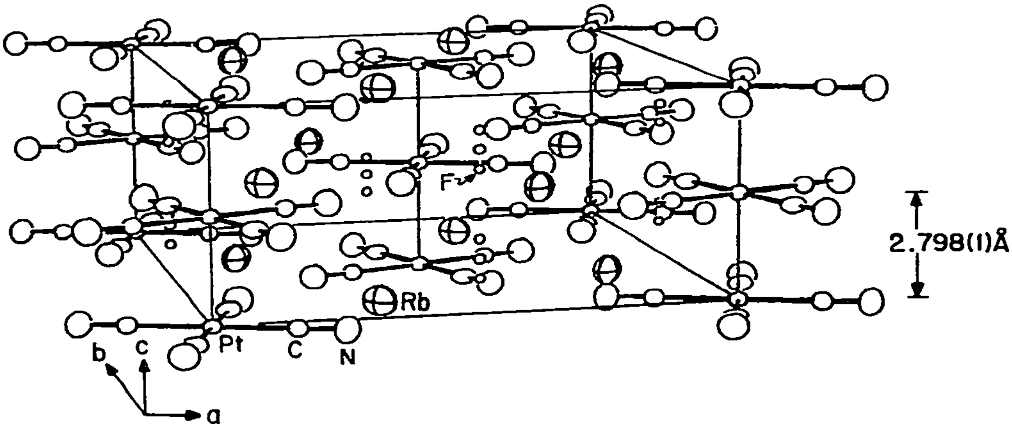

Fig. 1. A perspective view of the unit cell of $Rb_2[Pt(CN)_4](FHF)_{0.40}$. Partially occupied fluorine positions are indicated by small circles [18]. Permission granted by the N.Y. Academy of Sciences and authors.

Large disparities in anion/cation size generally promote hydration; for example, $RbPt(CN)_4Cl_{0.3}$ $r_{Rb^+}/r_{Cl^-} = 0.31$ and the result is a hydrated complex; in $CsPt(CN)_4Cl_{0.3}$ $r_{Cs^+}/r_{Cl^-} = 0.93$ and the resulting complex is anhydrous [18].

The intrachain and interchain Pt—Pt spacings in these compounds depend in part on the cation and anion size. An increase in cation and anion size has been observed to result in an increase in these distances according to X-ray crystallographic studies as shown in Table 2 [19]. Also, it would appear that as the degree of partial oxidation increases the inter- and intra-chain distances decrease, with a concomitant increase in electrical conductivity (Table 2). Further information concerning structural concepts and conductivities of partially oxidized tetracyanoplatinates (POTCP) is summarized in Table 3. For further discussion on these conductors see a recent review [20].

### *(iii) Planar, organic-metallic complexes*

The possibility of attaining highly conducting 1-D transition metal complexes with extended, higher molecular weight ligands was only recently realized. Phthalocyanines and tetrabenzporphins were found to form highly conducting 1-D systems upon $I_2$ oxidation. A variety of transition metals were found to take part in this reaction including Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Pt(II) according to the equation [3—5]

$$(MAC)M + \tfrac{1}{2}I_2 \rightarrow (MAC)MI$$

where MAC = macrocyclic ligand. Notable about this series is the occurrence of first row transition metals not of $d^8$ configuration. This aspect, along with the observation that the metal-free phthalocyanine exhibits analogous behavior, suggests that a different mechanism of electrical conduction other than that observed for the tetracyanoplatinates is in effect. Both resonance

TABLE 2

Comparison of DPO, intra- and inter-chain Pt—Pt spacings for several 1-D tetracyanoplatinates

| | DPO [a] | Pt—Pt (intra) (Å) | Pt—Pt (inter) (Å) |
|---|---|---|---|
| $K_2[Pt(CN)_4][Cl]_{0.3} \cdot 3\ H_2O$ | 2.3 | 2.87 | 9.883 |
| $Rb_2[Pt(CN)_4][Cl]_{0.3} \cdot 3\ H_2O$ | 2.3 | 2.90 | 10.142 |
| $K_2[Pt(CN)_4][Cl]_{0.3} \cdot 3\ H_2O$ | 2.3 | 2.87 | 9.883 |
| $K_2[Pt(CN)_4][Br]_{0.3} \cdot 3\ H_2O$ | 2.3 | 2.88 | 9.907 |
| $Cs[Pt(CN)_4][Cl]_{0.30}$ | 2.30 | 2.859 | 9.317 |
| $Cs[Pt(CN)_4][HFH]_{0.39}$ | 2.39 | 2.833 | 9.233 |

[a] Degree of partial oxidation.

TABLE 3

Crystal structure and conductivities for several Krogmann-type conductors [a]

| Conductor | Space group [b] | $d_{Pt-Pt}$(Å) (298 K) | Conductivity [c] ($\Omega^{-1}$ cm$^{-1}$) | Color |
|---|---|---|---|---|
| Pt metal | | 2.775 | $9.4 \times 10^4$ | Metallic |
| $K_2[Pt(CN)_4]Br_{0.30} \cdot 3\ H_2O$ | $P4mm$ | 2.89 | 4—1050 | Bronze |
| $K_2[Pt(CN)_4]Cl_{0.30} \cdot 3\ H_2O$ | $P4mm$ | 2.87 | ca. 200 | Bronze |
| $K_2[Pt(CN)_4]Br_{0.15}Cl_{0.15} \cdot 3\ H_2O$ | $P4mm$ | | | |
| $Rb_2[Pt(CN)_4]Cl_{0.30} \cdot 3\ H_2O$ | $P4mm$ | 2.877 and 2.924 | 10 | Bronze |
| $Cs_2[Pt(CN)_4]Cl_{0.30}$ | $I4/mcm$ | 2.859 | ca. 200 | Bronze |
| $(NH_4)(H_3O)_{0.17}[Pt(CN)_4]Cl_{0.42} \cdot 2.83\ H_2O$ | $P4mm$ | 2.910 and 2.930 | 0.4 | Bronze |
| $Cs_2[Pt(CN)_4](N_3)_{0.25} \cdot 0.5\ H_2O$ | $P\bar{4}b2$ | 2.877 | | Reddish-copper |
| $Rb_3(H_3O)_{0.x}[Pt(CN)_4](O_3SO \cdot H \cdot OSO_3)_{0.49} \cdot H_2O$ | $P\bar{1}$ | 2.826 | | Copper |
| $K_{1.75}[Pt(CN)_4] \cdot 1.5\ H_2O$ | $P\bar{1}$ | 2.965 and 2.961 | 115—125 | Bronze |
| $Rb_{1.75}[Pt(CN)_4] \cdot 1.5\ H_2O$ | d | 2.94 | 1 | Bronze |
| $Cs_{1.75}[Pt(CN)_4] \cdot 1.5\ H_2O$ | d | | | Bronze |
| $K_2[Pt(CN)_4](FHF)_{0.30} \cdot 3\ H_2O$ | $P4mm$ | 2.918 and 2.928 | | Reddish-bronze |
| $Rb_2[Pt(CN)_4](FHF)_{0.40}$ | $I4/mcm$ | 2.798 | 2300 | Gold |
| $Rb_2[Pt(CN)_4](FHF)_{0.26} \cdot 1.7\ H_2O$ | $C2/c$ | 2.89 | | Greenish-bronze |
| $Cs_2[Pt(CN)_4](FHF)_{0.39}$ | $I4/mcm$ | 2.833 | 1600 | Reddish-gold |
| $Cs_2[Pt(CN)_4](FHF)_{0.23}$ | $I4/mcm$ | 2.872 | 250—350 | Reddish-bronze |
| $Cs_2[Pt(CN)_4]F_{0.19}$ | $Immm$ | 2.886 | | Reddish-gold |
| $[C(NH_2)_3]_2[Pt(CN)_4](FHF)_{0.26} \cdot x\ H_2O$ | | 2.90 | | Bronze |
| $[C(NH_2)_3]_2[Pt(CN)_4]Br_{0.25} \cdot H_2O$ | $I4cm$ | 2.908 | | Bronze |

[a] Data taken in part from ref. 20. [b] For the space group $P4mm$ the Pt—Pt intrachain distances are not required to be equal, but often appear to be so. When they have been determined to be different both distances are tabulated. [c] Results are for a range of literature values for room temperature and by the four point probe d.c. conductivity method. [d] The crystal class is monoclinic but the space group is unknown. The lattice constants for the Cs salt are $a$ = 18.35 Å, $b$ = 5.760 Å, $c$ = 19.92 Å, $\beta$ = 109.03°; for the Rb salt the lattice constants are $a$ = 10.56 Å, $b$ = 33.2 Å, $c$ = 11.74 Å, $\beta$ = 114.23°.

Raman and $^{129}I$ Mössbauer studies indicate the form of the iodine to be mainly $I_3^-$ with negligible amounts of $I^-$ and $I_2$. EPR spectra indicate $g_{II}$ = 2.012 and $g_I$ = 2.006 with a narrow line width $Wpp$ = 5 G. Such values are analogous to those found in π-cation radical type species and are indicative of ligand oxidation. The conductivities of the complexes at room temperature range from 250 to 600 $\Omega^{-1}$ $cm^{-1}$ and are comparable to those of the purely organic metals TTF-TCNQ [4]. Temperature dependence studies confirm the metallic conductivity of these systems. As the temperature is lowered, conductivity increases to a maximum at approximately 90 K.

In systems such as the phthalocyanines, where a large cross sectional area is encountered, it becomes important to examine individual charge carriers and the mean free path of a carrier along a stacking direction [4,5]. The conductivity ($\sigma^{\pi}$) along the chain related to $A$, the cross sectional area, and λ, the mean free path becomes

$$\sigma^{II} = \frac{2\, e^2\lambda}{\pi\hbar A}$$

where $e$ = electronic charge and $\hbar = \frac{\text{Planck's constant}}{2\pi}$.

For NiPcI (Pc = phthalocyanine) λ ranges from 1.0 to 2.3 intermolecular spacings. This compares to 0.6 for the $K_2Pt(CN)_4Br_{0.3} \cdot 3\ H_2O$ and 0.4 to 0.6 for TTF-TCNQ although some of the highly conductive purely organic "metals" have considerably larger mean free paths such as 2.1 to 2.8 spacings for tetrathiatetracene tri-iodide. For nickel metal the mean free path is 24.

The structural aspects of the partially-oxidized phthalocyanines can be examined from data on NiPcI. Partially-oxidized nickel tetrabenzporphyrin can also be considered at this point since it behaves similarly to partially-oxidized nickel phthalocyanine. Both have similarly shaped ligands, Ni—Ni spacings of ca. 3.25 Å and indistinguishable structures [5]. Powder diffraction studies of other phthalocyanines $MPcI_x$ and $PcH_2I_x$ indicate similar structures. As is often the case with the 1-D complexes, the NiPcI crystallizes in the tetragonal space group ($P4mcc$). The cations and anions are stacked along the $c$ axis. Figure 2 shows a perspective view down the $c$ axis of the unit cell of NiPcI. Phthalocyanine groups along the chain are staggered by 39.5° from adjacent neighbors. Intermolecular phthalocyanine contacts along the chain direction are 3.244(3) Å [21]. Such a repeat distance would be considered far for $d_{z^2}$ interaction, but both the EPR data and the broad range of metals which are capable of forming these complexes indicate that ligand π orbital interactions are undoubtedly the major mechanistic contributors to the conductivity.

More recently a new series of 1-D phthalocyanine complexes has been reported. These are polysiloxane, polygermyloxane and polystannyloxane complexes of phthalocyanine [22], which, although not transition metals, should be mentioned. Upon $I_2$ oxidation these complexes form a wide range of dopant geometries. Resonance Raman measurements have shown $I_3^-$ presence

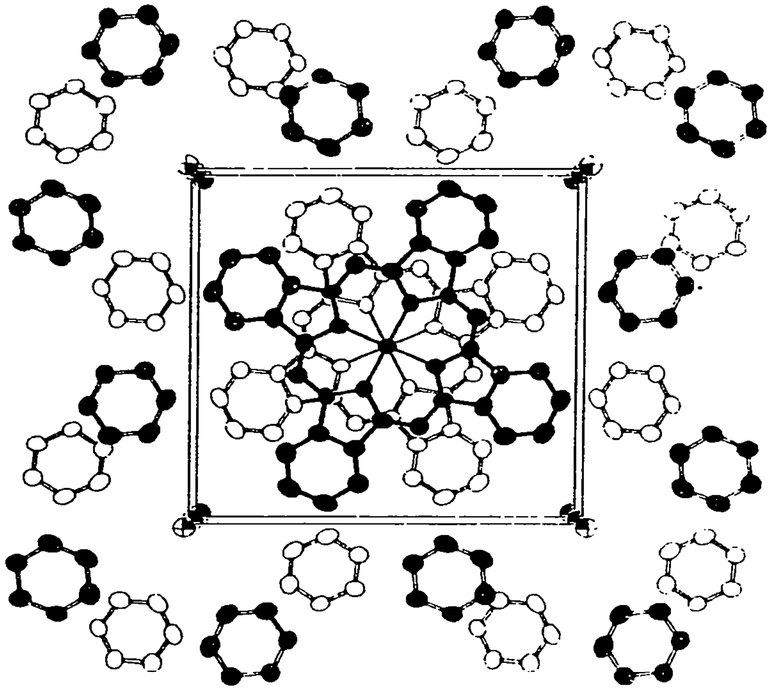

Fig. 2. View down the *c* axis of the unit cell of $\mathrm{NiPcI}_{1.0}$ [21]. Permission granted by the N.Y. Academy of Sciences and authors.

and no significant $I_2$ concentration. Large increases in electrical conductivity occur upon $I_2$ oxidation in the order of $\sigma_{\mathrm{Si}} \gtrsim \sigma_{\mathrm{Ge}} > \sigma_{\mathrm{Sn}}$. Powder diffraction studies show a tetragonal system with probably interplanar spacings of 3.33(2), 3.51(2) and 3.95(2) Å, respectively, for Si, Ge and Sn. Again the mechanism of conductivity would appear to be via ligand interactions and so, undoubtedly, the variation in the conductivities of this series is due to the different interplanar spacings.

### *(iv) Nonplanar, organic-metallic complexes*

A series of ligands of varying degrees of planarity comprises this group of compounds. Slight distortions from planarity are exemplified by the pseudomacrocyclic bis(glyoximates) such as bis(diphenylglyoximate), nickel(II) and palladium(II) [6—10]. In general, the complexes are insulators with $\sigma$ = ca. $10^{-12}$ $\Omega^{-1}$ $\mathrm{cm}^{-1}$ in their unoxidized form, and upon reaction with $I_2$ conductivity increases by a factor of ca. $10^6$ to the semiconductor range. For the partially-oxidized bis(glyoximate) systems it would appear that only the Ni(II) and Pd(II) analogs form the partially-oxidized complexes upon oxidation. The Pt(II) complexes are oxidized to Pt(IV). Conductivities for the unoxidized and oxidized complexes are shown in Table 3.

Structurally the bis(glyoximates) are more analogous to the phthalocyanine complexes rather than the tetracyanoplatinates. In the metal bis(diphenylglyoximates), square planar columns (staggered by 90°) are formed with disordered chains of iodine in channels parallel to the metal chains, surrounded by phenyl groups [23,24]. A perspective view down the c axis of the unit cell of the $Ni(dpg)_2(I)$ is illustrated in Fig. 3. The iodine exists as the $I_5^-$ ion, based on Raman and Mössbauer data. In the Ni compound the $Ni(dpg)_2$ units are considered to be in a fractional oxidation state of +0.2, and the Ni—Ni distances are reduced from 3.547 Å in the non-oxidized state, to 3.223 Å in the oxidized version. The compound is formulated as $Ni(dpg)_2(I_5)_{0.2}$. The bis(benzoquinone)dioximates are closely related to the diphenylglyoximates [25]. Stacks are found in the Pd compound, staggered by 65° and disordered chains of iodine in the chain direction. Pd—Pd distances are 3.184 Å in the oxidized form and 3.202 Å in the unoxidized form. The $Pd(bqd)_2$ units carry a residual +0.17 fractional charge. A $10^3$ to $10^4$ fold increase in electrical con-

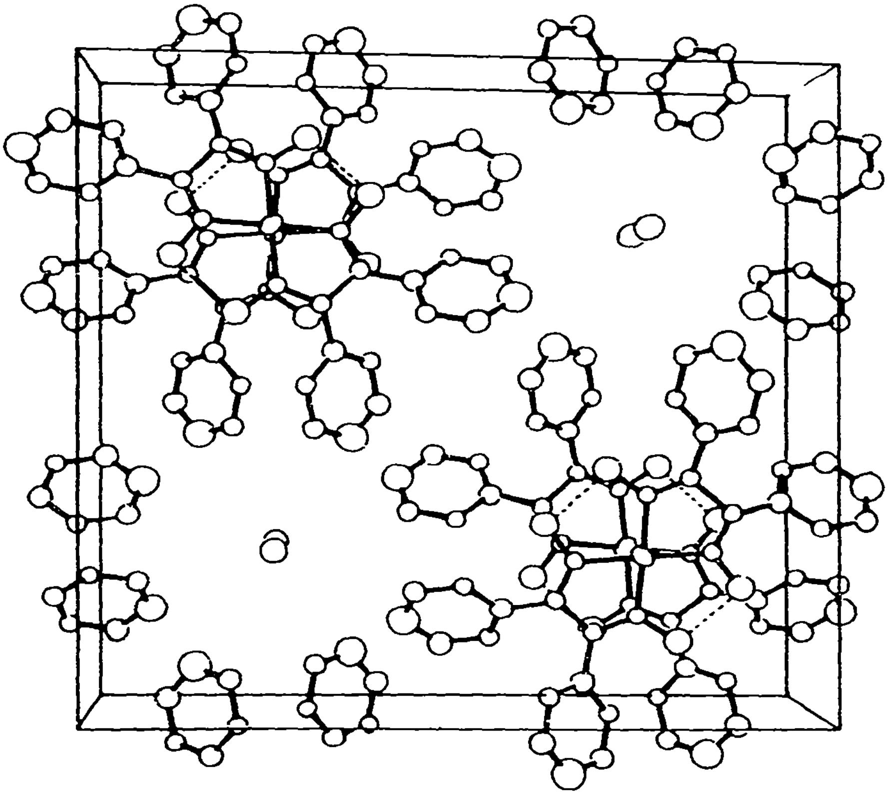

Fig. 3. Perspective view down the c axis of the unit cell of $Ni(dpg)_2I$. Dotted lines show the diphenylglyoximate O—H—O bonds [21,23,24]. Permission granted by the American Chemical Society and authors.

ductivity occurs upon oxidation but still the conductivities are in the semiconductor range.

In reviewing the dpg conductor in this class, we observe very little change occurring in conductivities and M—M distances as the metal changes (e.g., Ni → Pd). Polyiodides are considered to play only a minor role in charge transport. Compounds containing no metal but polyiodide chains demonstrate low conductivities. Also, $M(dpg)_2Br$ complexes show conductivities which are nearly identical to the $M(dpg)_2I$ conductors. It is thus presently considered that the $\pi$ systems in the ligand columns are the pathway for electrical conduction. Similar considerations can be made in the bis(benzoquinone)dioximate complexes.

Partially-oxidized 1,4,5,8,9,12,13,16-octamethylbenzporphinatonickel(II), $Ni(OMTBP)(I_3)_{0.36}$ has been recently structurally characterized by X-ray studies [16]. Methyl substitution of TBP increases the Ni—Ni spacing to ca. 3.77 Å from ca. 3.25 Å in the unsubstituted derivative. The room temperature conductivity is ca. 10 $\Omega^{-1}$ cm$^{-1}$, a value less than that of ca. 350 $\Omega^{-1}$ cm$^{-1}$ for the unmethylated complex $Ni(TBP)(I_3)_{0.33}$ [5]. $Ni(OMTBP)(I_3)_{0.36}$ crystallizes in the space group $D_{4h}^{11}$, $P4/nbc$ of the tetragonal system with four formula units per cell. The structure consists of ruffled macrocycles stacked with relatively large intermolecular spacings along the $c$ axis (Ni—Ni = 3.778(5) Å). Chains of severely disordered linear $I_3^-$ units are parallel to the stacking axis between adjacent macrocycle columns. Intermolecular spacings do play a major role in the achievement of highly conducting systems; however, at least in the case of ligand based conductors, the degree of partial oxidation appears to be a predominant factor. The $Ni(OMTBP)(I_3)_{0.36}$ is, as expected from the longer intermolecular spacings, less highly conducting than its parent $Ni(TBP)(I_3)_{0.33}$. The fact that it displays an unexpectedly large conductivity in the metallic range, despite its unfavorable stacking distances, must rest with the aspect of nonintegral oxidation states.

More drastic distortions are encountered in macrocyclic complexes of Pd(II) and Pt(II) with TAAB (nonplanar, saddle-shaped macrocyclic ligand, tetrabenzo [b,f,j,n][1,5,9,13] tetraazacyclohexadecine), which have recently been reported to form more highly conducting complexes upon reaction with $I_2$ [26,27]. The resulting lustrous, metallic, dark red needles exhibit the stoichiometry $[M(TAAB)][I_8]$ where M = palladium(II) and platinum(II). In contrast to the previously discussed complexes only integral oxidation states are involved. As expected from the considerations discussed above, the conductivities are greatly decreased. X-ray data has confirmed the presence of the octaiodide dianion [28] indicating that the macrocyclic complex has not undergone oxidation, unlike the previously discussed systems. Within the macrocyclic cation the immediate coordination sphere of the metal is nearly planar; however, the overall geometry of the macrocyclic complex conforms to a hyperbolic paraboloid with cavities of 2.68 Å about the axial metal sites (Fig. 4). The anion consists of discrete Z-shaped nonplanar chains of $I_8^{2-}$ composed of two $I_3^-$ units weakly associated with an elongated $I_2$. The conductivity

TABLE 4

Some physical properties of 1-D conductors [a]

| Conductors | Color | $d$(M—M) (Å) | $\Delta$ [a] (Å) | Oxidized $\sigma(\Omega^{-1}\ \mathrm{cm}^{-1})$ | Non-oxidized $\sigma(\Omega^{-1}\ \mathrm{cm}^{-1})$ | $R$ [b] | Predominant conductive mechanism |
|---|---|---|---|---|---|---|---|
| (1) 1-D tetracyanoplatinates | Bronze, copper, gold | <2.96 | 0.7 | $10^3$ | $10^{-7}$ | $10^{10}$ | Metal—metal centered |
| Pt—Pt in metal | | 2.775 | | $9.4 \times 10^4$ | | | |
| (2) Planar, organic-metallic (e.g. NiPcI) | Silver-gold | 3.244 | [c] | 1 | $10^{-11}$ | $10^{11}$ | Ligand—ligand centered |
| Ni—Ni in metal | | 2.49 | | $1.46 \times 10^3$ | | | |
| (3) Distorted, organic metallic (e.g. $\mathrm{Ni(dpg)_2(I_5)_{0.2}}$) | Bl-gold | 3.22 | 0.32 | $2\text{—}11 \times 10^{-3}$ | $<8 \times 10^{-9}$ | ca. $10^7$ | Ligand—ligand centered |
| Pd—Pd in metal | | 2.751 | | $9.26 \times 10^4$ | | | |

[a] $\Delta = d$(M—M) (non-oxidized) $- d$(M—M) (oxidized). [b] $R$ = oxidized $\sigma$/non-oxidized $\sigma$. [c] Comparison meaningless since Ni(Pc) does not stack.

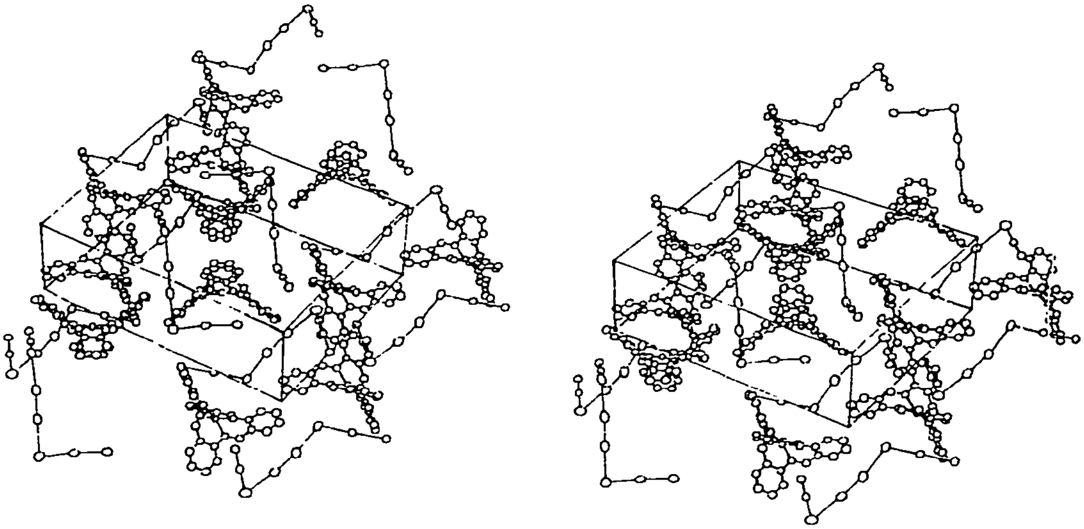

Fig. 4. Packing diagram for $Pd(TAAB)(I)_8$ viewed down the *Z* axis (slightly rotated) with *X* vertical [28].

in the semiconductor range is thought to occur via macrocycle-$I_3^-$ interactions.

Single crystal conductivity measurements indicate relatively low conductivities compared to the partially-oxidized tetracyanoplatinates and phthalocyanines as shown in Table 4. An interesting effect is observed upon the application of pressure, however. For the Pd-TAAB complex up to 1000-fold increases in conductivity are observed at pressures of 10 kbar as shown in Table 5. Pressure studies of conductivity have been made for some of the unoxidized bis(glyoximates) [29]. Here also a large relationship of electrical resistivity with pressure has been noted. Minima in electrical resistivities are found to occur at 193 kbar for bis(dimethylglyoximato)platinum(II). No data were reported for the 0—10 kbar region.

TABLE 5

Conductivity measurements for $M(TAAB)^{n+}$

| Complex | Conductivity ($\Omega^{-1}$ cm$^{-1}$) | | | |
|---|---|---|---|---|
| | Single Crystal | Powder (1 bar) | Powder (5 kbar) | Powder (10 kbar) |
| $[Pd(TAAB)][BF_4]_2$ | | $1 \times 10^{-9}$ | $1 \times 10^{-8}$ | $8 \times 10^{-10}$ |
| $Pd(TAAB)(I)_8$ | $10^{-7}$ | $1 \times 10^{-7}$ | $4 \times 10^{-6}$ | $5 \times 10^{-5}$ |
| $[Pt(TAAB)][BF_4]_2$ | | $1 \times 10^{-9}$ | $1 \times 10^{-7}$ | $2 \times 10^{-7}$ |
| $Pd(TAAB)(I)_8$ | $10^{-4}$ | $6 \times 10^{-7}$ | $6 \times 10^{-6}$ | $6 \times 10^{-6}$ |

## C. SUMMARY

1. Structural characteristics have been employed to separate square planar one-dimensional complexes into three classes. The influence of the ligand systems, metal ions, electronic, steric and valency aspects, and their correlation with structure and conductivity have been considered. The compounds all contain partially-oxidized species and the classes are as follows: (a) predominantly planar tetracyanoplatinates with close intermolecular spacings; (b) transition metal complexes with extended ligand systems which are still predominantly planar but with longer intermolecular separations; and (c) non-planar complexes with extended ligand systems which, in some instances display even longer intermolecular distances.

2. Partial oxidation and intermolecular proximity are of tantamount importance. The former would appear to be a prerequisite, while the latter is somewhat more flexible (e.g. Ni(OMTBP)$(I_3)_{0.36}$).

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