One-dimensional Metallic Complexes

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1 Introduction

A one-dimensional (1-D) metal may be defined as a material which exhibits metal-like properties along one direction of a crystal and non-metallic properties orthogonal to this direction. For the past decade there has been great activity concerning compounds of this type because of interest in the theoretical, chemical, and solid state properties of highly conducting anisotropic materials and their potential technological applications. 1-D metals require a very stringent combination of structural and electronic properties. Within the crystal structure the molecules must be arranged along one direction with a short inter-molecular distance and in such a way that effective inter-atomic or inter-molecular orbital overlap can occur with the neighbouring molecules in this direction. This structural feature must extend throughout the crystal and not be present just in isolated dimeric or trimeric units. No comparable overlap of orbitals must exist orthogonal to the stacking direction. Facile electron transport will arise in the preferred direction only either from the existence of a partially filled band or from reduced Coulombic interactions which will allow easy electron transport between localized centres along the conducting axis. Both the structural and the electronic properties of these materials are strongly dependent on the chemical nature of the molecules and ions comprising the lattice, and subtle changes in the chemical composition of the lattice can produce dramatic effects on the properties of two otherwise chemically similar materials.

The several classes of 1-D metals known at present include organic metals (*e.g.* TTF–TCNQ),[1] main-group element polymers [*e.g.* $(SN)_x$],[2] and organic polymers [*e.g.* $(CHI_{0.25})_x$][3] but this review is concerned with 1-D metals in which the metallic properties are due to a chain of interacting metal atoms with short intra-chain metal–metal distances (< 3.0 Å). This class of 1-D metal we term '1-D Metallic Complexes'. Excluded from the review are those systems [*e.g.* $NiPc(I_3)_{0.33}$ where Pc = phthalocyanine] which also contain chains of metal atoms but with much larger intra-chain metal–metal distances (> 3.0 Å) and in

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[1] A. J. Heeger in 'Highly Conducting One-Dimensional Solids', ed. J. T. Devreese, R. P. Evrard, and V. E. Van Doren, Plenum Press, New York, 1979, p. 69.

[2] M. M. Labes, P. Love, and L. F. Nichols, *Chem. Rev.*, 1979, **79**, 1.

[3] C. K. Chiang, A. J. Heeger, and A. G. MacDiarmid, *Ber. Bunsenges. Phys. Chem.*, 1979, **83**, 407.

which the 1-D metallic properties arise predominantly from intra-chain ligand–ligand interactions.[4]

The first examples of 1-D metallic complexes were prepared in the first half of the 19th century.[5,6] However, they were not recognized as 1-D metals until the work of Krogmann and co-workers in the 1960s.[7] Since that time a number of reviews have appeared concerned mainly with the physics[8,9,10] or chemistry[11,12,13] of these complexes, including a very comprehensive one by Miller and Epstein[14] of the work up to 1975. Several up-to-date and comprehensive articles on 1-D metallic complexes will appear in a book to be published shortly.[15] This present review will not attempt to be comprehensive but will present an overview of the field for the general reader with particular reference to the advances made since 1975.

2 Chemistry of 1-D Metallic Complexes

In the case of co-ordination compounds the structural requirements for a 1-D metal are satisfied by square-co-planar complexes which can stack above one another to form a columnar stacked structure (Figure 1). The ligands surrounding the metal atoms ensure that the inter-chain separation is large, usually greater than 9 Å, compared with the average intra-chain metal–metal distance ($d_{\mathrm{M-M}}$) which is usually less than 3 Å. This very large difference between the intra- and inter-chain metal–metal separation results in much higher degrees of anisotropy in this class of 1-D metal compared with the other classes of 1-D metals mentioned in the introduction.

Square-co-planar complexes are commonly found for metal ions with a d^8 configuration and many examples of columnar stacked structures are known for these ions.[11] The effective overlap of metal-atom orbitals with those of neighbouring metal atoms in the chain will increase with increasing spatial extension of the orbitals. Thus most 1-D metallic complexes are found for $\mathrm{Pt^{II}}$ and $\mathrm{Ir^{I}}$ where the d^8 configuration is associated with a combination of the large $5d$ orbitals and a relatively low oxidation state. For the same reason the best known examples of 1-D metallic complexes involve anionic rather than cationic complex ions.

Although the choice of the central metal atom is crucial for the formation of a 1-D metal, the choice of the ligands is also very important. At present, 1-D metallic complexes are known only with ligands containing atoms from the first

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[4] B. M. Hoffman, T. E. Phillips, C. J. Schramm and S. K. Wright in 'Molecular Metals', ed. W. E. Hatfield, NATO Conference Series: VI, Materials Science, Plenum Press, New York, 1979, Vol. 1, p. 393.

[5] W. Knop and G. Schneidermann, *J. Prakt. Chem.*, 1846, **37**, 462.

[6] J. W. Döbereiner, *Pogg. Ann.*, 1833, **28**, 180.

[7] K. Krogmann, *Angew. Chem. Internat. Edn. Engl.*, 1969, **8**, 35, and references therein.

[8] H. R. Zeller, *Progr. Solid State Phys.*, 1973, **13**, 31.

[9] G A. Toombs, *Phys. Rep.*, 1978, **40**, 181.

[10] R. H. Friend and D. Jérome, *J. Phys. C.*, 1979, **12**, 1441.

[11] T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, 1972, **1**, 99.

[12] J. M. Williams and A. J. Schultz in ref. 4, p. 337.

[13] G. D. Stucky, A. J. Schultz, and J. M. Williams, *Annu. Rev. Mater. Sci.*, 1977, **7**, 301.

[14] J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, 1976, **20**, 1.

[15] 'Extended Linear Chain Compounds', ed J. S. Miller, Plenum Press, to be published.

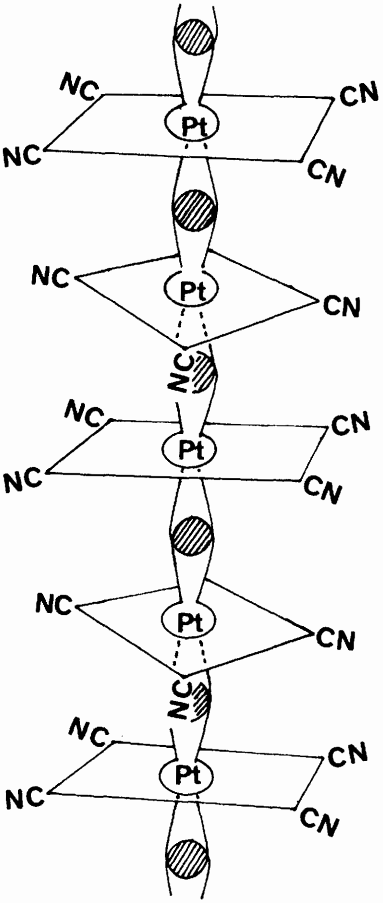

Figure 1 *Columnar stacked structure of* $[Pt(CN)_4]^{x-}$ *ions, showing overlap of platinum* $5d_{z^2}$ *orbitals*

short period. These atoms are presumably small enough to allow the short d_{M-M} required for effective metal orbital overlap. The bonding characteristics of the ligand are also very important, and π-acceptor ligands [*e.g.* CO, CN^-, and $(C_2O_4)^{2-}$] which can remove electron density from the central metal atom and thus reduce coulombic repulsions between adjacent metal atoms appear to be favoured.

Krogmann discussed the metallic properties of this class of compound in terms of a partially filled 1-D band in the metal-atom chain direction.[7] In the columnar stacked structure orbital overlap can occur between d_{z^2}, p_z, and to a lesser extent the d_{xz}, d_{yz}, and $d_{x^2-y^2}$ orbitals of the metal atoms. If the metal atoms are close enough this will result in the formation of a 1-D band throughout the length of the crystal, and if the band is only partially filled 1-D metallic properties will be found in the chain direction. Since an ion with a d^8 configuration possesses an even number of electrons a partially filled band can arise only if:

(a) overlap occurs between the highest energy filled and the lowest energy empty bands [Figure 2(a)]

or (b) electrons are removed from the top part of the filled band of highest energy, *i.e.* partial oxidation of the d^8 ion [Figure 2(b)].

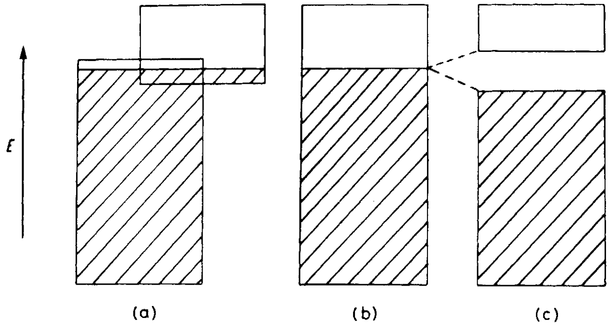

Figure 2 *Simple band structure of a* 1-*D metallic complex:* (a), *overlap of full and empty bands;* (b), *partially filled band;* (c), *splitting of partially filled band by the Peierls distortion*

Of the compounds studied so far mechanism (b) involving a partially filled d_{z^2} band is most commonly found, but (a) has been proposed as a possible explanation for the properties of certain complexes whose analysis suggests that they are not partially oxidized [*e.g.* $IrCl(CO)_3$].[16]

There is an extensive range of d^8 integral oxidation state tetracyanoplatinate(II) salts which are precursors for partially oxidized complexes.[11] These d^8 complexes have $d_{Pt-Pt} \geqslant 3.09$ Å and exhibit semiconducting behaviour with $\sigma_{\parallel}$, the d.c. specific conductivity in the platinum-atom chain direction, of $< 10^{-4}\ \Omega^{-1}\,cm^{-1}$ at room temperature.[17] Partial oxidation of some of these salts results in complexes with a much reduced d_{Pt-Pt} (<2.9 Å) and exhibiting metallic behaviour parallel to the platinum-atom chain direction at room temperature. A selection of well characterized, partially oxidized 1-D metallic complexes is shown in the Table. Most examples of this type of 1-D metal contain platinum with either CN^- or $(C_2O_4)^{2-}$ ligands.

In general there are two basic types of partially oxidized complexes.

A. Anion-deficient (AD) Salts.—In these salts the additional positive charge on the Pt atoms due to partial oxidation is compensated by the incorporation of a non-stoicheiometric number of anions compared with the parent Pt^{II} complex.

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[16] A. H. Reis and S. W. Peterson, *Ann. N.Y. Acad. Sci.*, 1978, **313**, 560.

[17] J. H. O'Neill, A. E. Underhill, and G. A. Toombs, *Solid State Commun.*, 1979, **29**, 557.

Table *Properties of selected* 1-*D metallic complexes*

Compound	*{abbreviation}*	*DPO*	*Space group*	d_{Pt-Pt} /Å	$\sigma_{\parallel}$ (d.c.) /Ω^{-1} cm^{-1} (room temperature)	Δ /meV	T_{3D} /K
Pt metal				2.774	9.4×10^4		
AD Salts[a]							
$K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$	{KCP(Br)}	0.30	*P4mm*	2.89	300	72	100
$(NH_4)_2(H_3O)_{0.17}[Pt(CN)_4]Cl_{0.42}\cdot 2.8H_2O$	{ACP(Cl)}	0.25	*P4mm*	2.910(5) 2.930(5)	0.4	125	195
$Rb_2[Pt(CN)_4](FHF)_{0.4}$	{RbCP(FHF)}	0.4	*I4/mcm*	2.798(1)	2300	20	80
$Cs_2[Pt(CN)_4]Cl_{0.3}$	{CsCP(Cl)}	0.30	*I4/mcm*	2.859(2)	200	30	90
CD Salts							
$K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$[b]	{K(def)CP}	0.25	*P*1	2.961(1)	5—100	55	—
$Rb_{1.67}[Pt(C_2O_4)_2]\cdot 1.5H_2O$[c]	{Rb–OP}	0.33	*P*1	2.717 2.830 3.015	7×10^{-3}	77	>298 ($T_{NP} > 298$)
$Co_{0.83}[Pt(C_2O_4)_2]\cdot 6H_2O$[d]	{Co–OP}	0.30	*Cccm*	2.841	2—25	50	295 ($T_{NP} \sim 300$)
$Mg_{0.82}[Pt(C_2O_4)_2]\cdot 6H_2O$[d]	{Mg–OP}	0.30	*Cccm*	2.85	0.2—50	50—85	<97 ($T_{NP} = 284$)

[a] refs. 12 and 31. [b] ref. 56. [c] ref. 49. [d] ref. 51.

These salts have the general formula $M_m[PtL_4]X_n{\cdot}pH_2O$ [where M is a cation and X an anion, *m* is an integer (1, 2, or 3) and *n* a non-integer (0.19 to 0.49)].

B. Cation-deficient (CD) Salts.—In these salts a non-stoicheiometric deficiency of cations compared with the parent Pt^{II} complex compensates for the partial oxidation of the platinum atoms. The general formula is therefore $M_m[PtL_4]{\cdot}pH_2O$ (where *m* is a non-integer). For monovalent cations $m = 1.62$ to 1.81 and for divalent cations $m = 0.81$ to 0.84.

The successful characterization and study of the structural and solid-state properties of complexes of this type require the growth of well formed single crystals. The predominance of the tetracyanoplatinate and bis(oxalato)platinate complexes in this field is mainly because they can be readily crystallized from aqueous solution. A series of partially oxidized AD and CD dicarbonyldichloroiridate salts also exists, but unfortunately they have been prepared and studied only as polycrystalline powders.[14,18]

A variety of methods have been used to prepare well formed crystals of the partially oxidized platinum complexes and some of these have been described recently in *Inorganic Syntheses*.[19]

Chemical Oxidation. In 1846 Knop and Schneidermann[5] reported that oxidation of a solution of $K_2[Pt(CN)_4]{\cdot}3H_2O$ with a small quantity of bromine gave copper coloured needles upon crystallization. This product is now known to be $K_2[Pt(CN)_4]Br_{0.30}{\cdot}3H_2O$ [KCP(Br)] and can be prepared also from solutions containing $K_2[Pt(CN)_4]{\cdot}3H_2O$ and $K_2[PtBr_2(CN)_4]$ in the mole ratio of 5:1. Large crystals ($> 2 \times 1 \times 1$ cm^3) can be grown from aqueous solutions containing small amounts of KBr and urea.[20] Extensive investigations have shown that the stoicheiometry and the degree of partial oxidation (DPO) of this product is constant, irrespective of the mole ratio of the starting materials. A number of other compounds which are isostructural with KCP(Br) but containing Cl^- and either K^+, Rb^+, or NH_4^+ have been obtained in a similar way.[19,21] The treatment of solutions of the tetracyanoplatinate(II) salts with insufficient oxidizing agent to oxidize completely the platinum to Pt^{IV} has been used extensively in the preparation of partially oxidized complexes. For example, the treatment of an aqueous solution of $K_2[Pt(CN)_4]{\cdot}3H_2O$ with nitric acid produces the CD salt $K_{1.75}[Pt(CN)_4]{\cdot}1.5H_2O$, H [K(def)CP].[19]

Electrolytic Oxidation. Williams and co-workers[12] have shown that electrolytic oxidation of solutions containing $[Pt(CN)_4]^{2-}$ using platinum electrodes can produce a much wider range of salts than can be obtained using chemical oxidation. Both AD {*e.g.* $Rb_2[Pt(CN)_4](FHF)_{0.4}$} and CD [*e.g.* K(def)CP] salts have been produced by this method, which has been particularly valuable for the

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[18] A. P. Ginsberg, J. W. Koepke, J. J. Hauser, K. W. West, F. J. Di Salvo, C. R. Sprinkle, and R. L. Cohen, *Inorg. Chem.*, 1976, **15**, 514.

[19] *Inorg. Synth.* 1979, **19**, 1—22; *ibid.*, 1980, **20**, 20—33.

[20] R. B. Saillant, R. C. Jaklevic, and C. D. Bedford, *Mat. Res. Bull.*, 1974, **9**, 289.

[21] A. E. Underhill and D. J. Wood, *Ann. N.Y. Acad. Sci.*, 1978, **313**, 516.

production of a number of anhydrous materials. It is also a valuable method for the production of crystals of rather insoluble compounds because a very slow and controlled rate of oxidation can be achieved.

Aerial Oxidation. Concentrated yellow aqueous solutions of $H_2[Pt(C_2O_4)_2]$ quickly turn deep blue in the presence of atmospheric oxygen due to the formation of the partially oxidized acid $H_{1.6}[Pt(C_2O_4)_2]$.[22] In the presence of other cations this oxidation produces CD bis(oxalato)platinate salts as well formed single crystals.[23,24] Aerial oxidation is also used in the preparation of the CD dicarbonyldichloroiridate salts.

The determination of the oxidation state of the central metal atom in these complexes is very important since the fundamental solid-state properties are strongly dependent on the DPO of the Pt atoms. The DPO of the metal can be determined in several ways:

(i) From the mole ratio of the cations to anions found by conventional chemical analysis. This ratio may be misleading since compounds grown from acidic solutions may in some cases contain either protons, or protons plus additional anions, in the lattice.[25]

(ii) From the ratio of Pt^{IV} to Pt^{II}, determined iodimetrically in a solution of the complex.

(iii) From diffuse *X*-ray scattering (DXS) experiments described in Section 3. This is probably the most reliable and accurate method.[26,27]

3 Physics of 1-D Metallic Complexes

The simple band picture presented by Krogmann [Figure 2(b)] is useful to chemists for understanding the existence of partially oxidized compounds and their relationship to the unoxidized parent salts.[7] It is, however, far too simplistic to account for the detailed structural and solid-state properties observed in these materials. To understand these features it is necessary to consider briefly the physics of a 1-D metal which has been discussed in detail elsewhere.[8–10]

Chemists are very familiar with the Jahn–Teller theorem which states that any non-linear molecular system in a degenerate electronic state will be unstable and will undergo some kind of distortion that will lower its symmetry and split the degenerate state, thus lowering the total electronic energy of the system. R. E. Peierls[28] predicted, in a similar fashion, that a 1-D system possessing a partially occupied band would be inherently unstable with respect to a lattice distortion in the metal-atom chain direction (Figure 3). This distortion would split the band

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[22] K. Krogmann and P. Dodel, *Chem. Ber.*, 1966, **99**, 3408.
[23] A. J. Schultz, A. E. Underhill, and J. M. Williams, *Inorg. Chem.*, 1978, **17**, 1313.
[24] A. E. Underhill, D. M. Watkins, and C. S. Jacobsen, to be published.
[25] D. J. Wood and A. E. Underhill, *J. Chem. Soc., Dalton Trans.*, 1980, 360.
[26] R. Comès, M. Lambert, and H. R. Zeller, *Phys. Status Solidi B*, 1973, **58**, 587.
[27] A. Braude, A. Lindegaard-Andersen, K. Carneiro, and A. Steen Petersen, *Solid State Commun.*, 1980, **33**, 365.
[28] R. E. Peierls in 'Quantum Theory of Solids', Oxford University Press, Oxford, 1955, p. 108.

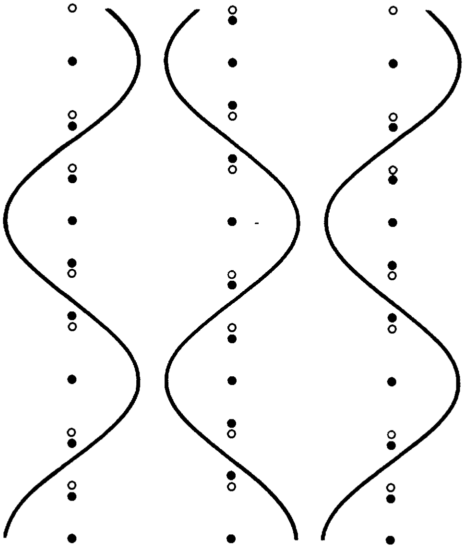

Figure 3 *Peierls distortion and associated charge density waves in* 1-*D metal-atom chains showing* 3-*D ordering between chains*
(Reproduced by permission from *Phys. Rep.*, 1978, **40**, 203)

into filled and empty bands of lower and higher energy respectively, thus lowering the total electronic energy of the system [Figure 2(c)]. The period of the distortion will depend upon the degree of band filling and hence on the DPO of the complex. The greater the distortion of the atoms from their mean positions the larger the band gap between the highest filled and lowest empty band, and hence the lower the electronic energy of the system. However, any distortion of the metal-atom chain has to be done against the restoring forces of the lattice. Hence the extent of the distortion and the size of the band gap will be a compromise between these two opposing effects. Thus the Peierls distortion (PD) converts a 1-D metal into an insulator or semiconductor by opening up a band gap at the Fermi surface. The band gap in the semiconducting region is twice the activation energy for conduction (Δ) and hence can be obtained from variable-temperature electrical-conduction studies. Alternatively it can be obtained from optical measurements. However, Peierls' argument is for the zero-temperature case. At finite temperatures well above absolute zero the band gap becomes temperature dependent and at some higher scale temperature (T_P) the band gap will disappear and the system will be metallic and undistorted.

When the degree of band filling is a simple fraction then the periodicity of the PD will be a small and simple multiple of the d_{M-M}. In this case the PD is said to be commensurate with the lattice, and the unit cell determined by conventional X-ray or neutron scattering studies will therefore accurately describe the PD as in $Rb_{1.67}[Pt(C_2O_4)_2]\cdot 1.5H_2O$ [Section 4B(ii)]. If the degree of band filling is not a small and simple fraction then the PD will not be a simple multiple of d_{M-M} and the coincidence of the position of the metal atom in the fundamental lattice and in the PD lattice will occur only after a large number of metal atoms. In this case the PD is said to be incommensurate with the fundamental lattice, and conventional structural studies will reveal only the average (undistorted) positions of the atoms in the fundamental lattice.

Experimentally the PD may be studied by diffuse X-ray scattering experiments (DXS). Since the PD is a 1-D distortion, the diffracted X-rays arising from it are observed as weak continuous lines on either side of the layer lines of the strong Bragg spots. The repeat distance of the PD is obtained from the relative position of the diffuse line and the Bragg spots. The DPO for the platinum complexes can be calculated from the relationship DPO $= 2(1 - \boldsymbol{k}_F d_{Pt-Pt}/\pi)$, where $2\boldsymbol{k}_F$ is the wave vector of the PD.

In the Peierls distorted state the electron density of the valence electrons is perturbed by the displacement of the positive platinum nuclei from their undistorted positions. Thus, instead of a uniform distribution of electron density along the metal-atom chain there will be a variation of electron density in phase with the lattice distortion. This is known as a charge-density wave (CDW, Figure 3). The lattice and charge-density displacements are totally interdependent and it is not possible to separate the two effects. In the commensurate case the PD/CDW is pinned to the underlying lattice and is therefore static. In theory, in the incommensurate case the PD/CDW is not fixed at any point in 1-D space and can move relative to the underlying lattice. In this case the PD is described as a dynamic distortion. However, an incommensurate PD/CDW may also be static if it is pinned to the underlying lattice by random electrostatic potentials. In the partially oxidized complexes random electrostatic potentials can arise in the lattice through lattice defects, impurities, and most importantly through the presence of a non-stoicheiometric number of ions distributed randomly amongst possible crystallographic sites. The presence of the random electrostatic potentials in the lattice will tend to pin the CDW, and hence the associated PD, into preferred positions within the lattice. Whether or not these random potentials will, in practice, pin the CDW and the relative importance of random potentials on the electronic properties of each compound can only be found by experiment. Diffuse X-ray scattering experiments yield no information about the dynamic properties of the PD, but inelastic neutron scattering experiments which study the vibrations (phonons) of the lattice can distinguish between a static and a dynamic PD. A dynamic CDW could contribute to the electrical conductivity of the material and it has been suggested by Fröhlich[29] that it could be a mechanism for superconductivity.

In a perfectly 1-D system a phase change can occur only at 0 K and it is through the presence of weak 3-D effects that real compounds exhibit metal–semiconductor transitions at finite temperatures. In the 1-D metallic complexes the

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[29] H. Fröhlich, *Proc. R. Soc. London, Ser. A*, 1955, **223**, 296.

chains of metal atoms are surrounded by ligands, cations, other metal-atom chains, and often other anions and water molecules. These systems are therefore not strictly 1-D but really 3-D with a large degree of anisotropy. These 3-D effects are very important and have allowed chemists to control and modify the properties of 1-D metallic complexes. In real 1-D metallic complexes the following temperature dependence of properties will be expected. At temperatures well above the scale temperature, T_P, the PD and the associated CDW disappear and the system behaves as a 1-D metal. At and below this temperature, critical fluctuations in electron density occur and create 1-D correlated domains over portions of the metal-atom chains. These fluctuations, which are the forerunners of the CDW, become increasingly important as the temperature is lowered. At a still lower temperature inter-chain Coulombic interactions become sufficiently strong to cause 3-D ordering of the CDWs on adjacent chains (Figure 3). The temperature at which this occurs is known as the three-dimensional ordering temperature T_{3D}. The inter-chain coupling parameter η is a measure of the 3-dimensionality of the lattice. The 3-D coupling can be visualized in terms of a static Coulombic coupling of the lattice or, in terms of an electron hopping from chain to chain, depending on the nature of the lattice.[30,31]

4 Properties of 1-D Metallic Complexes

The partially oxidized complexes exhibit many properties that characterize them as 1-D metals. Optical studies have shown that the striking metallic lustre observed for light polarized parallel to the metal-atom chains in KCP(Br) is due to a plasma edge which is characteristic of a metal.[32] These properties are consistent with nearly free-electron-like behaviour. Orthogonal to the metal-atom chain direction, KCP(Br) behaves as a transparent insulator. Similar results have been observed for K(def)CP[33] and $Zn_{0.81}[Pt(C_2O_4)_2]\cdot 6H_2O$, (Zn–OP).[34] Further evidence for the 1-D metallic nature of these materials is given by n.m.r., e.s.r., and magnetic susceptibility measurements.[14]

Metallic conductors such as copper and platinum typically have specific electrical conductivities in the range 10^5—10^6 Ω^{-1} cm^{-1} at room temperature. As shown in the Table (p. 433) the specific conductivities in the platinum-atom chain direction, $\sigma_{\parallel}$, of the partially oxidized complexes are considerably less than these values. The highest value, 2.3×10^3 Ω^{-1} cm^{-1}, is observed for $Rb_2[Pt(CN)_4](FHF)_{0.4}$.[35] Since the density of the metal atoms in the 1-D metallic complexes is only approximately 1/10th of that found in the metal itself, the observed $\sigma_{\parallel}$ should be increased by an order of magnitude to obtain a valid comparison of the relative transport properties of the metal atoms in the two

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[30] K. Carneiro, A. Steen Petersen, A. E. Underhill, D. J. Wood, D. M. Watkins, and G. A. Mackenzie, *Phys. Rev.* (*B*), 1979, **19**, 6279.

[31] A. E. Underhill, D. J. Wood, and K. Carneiro, *Synthetic Metals*, 1979/80, **1**, 395.

[32] P. Brüesch, S. Strässler, and H. R. Zeller, *Phys. Rev* (*B*), 1975, **12**, 219.

[33] R. L. Musselman and J. M. Williams, *J. Chem. Soc.*, *Chem. Commun.*, 1977, 186.

[34] A. E. Underhill, D. M. Watkins, and C. S. Jacobsen, *Solid State Commun.*, 1980, **36**, 477.

[35] D. J. Wood, A. E. Underhill, A. J. Schultz, and J. M. Williams, *Solid State Commun.*, 1979, **30**, 501.

systems. In the partially oxidized salts the anisotropy ratio $\sigma_{\parallel}/\sigma_{\perp}$ (where $\sigma_{\perp}$ is the specific conductivity perpendicular to the chain) can be as high as 10^5. There is, however, a great variation from compound to compound, not only in the magnitude of $\sigma_{\parallel}$ at room temperature (10^3—10^{-3} Ω^{-1} cm^{-1}) but also in the temperature dependence of $\sigma_{\parallel}$. These properties can be understood in detail only in terms of the composition and structural properties of these complexes.

It is convenient to discuss the properties of the known, partially oxidized 1-D metallic complexes within their anion-deficient (AD) and cation-deficient (CD) sub-groups.

A. Anion-deficient Salts.—There are two main types of structure adopted by the AD tetracyanoplatinate salts. The hydrated salts have primitive tetragonal lattices *P4mm*, whilst most of the anhydrous salts, and salts with a low degree of hydration, have body-centred tetragonal lattices *I4/mcm* (see Table).

(i) *Hydrated AD Tetracyanoplatinate Salts.* The structures and properties of these salts are best illustrated by $K_2[Pt(CN)_4]Br_{0.30}\cdot 3H_2O$, [KCP(Br)]. In this compound the DPO indicates that 0.30 electrons per platinum atom have been removed from the highest filled band (predominantly $5d_{z^2}$) to leave 1.70 electrons per platinum atom in the band. The structure of KCP(Br) contains columnar stacks of $[Pt(CN)_4]^{1\cdot 7-}$ ions with a linear Pt-atom chain aligned along the *c*-axis of the unit cell[36] (Figure 4). The d_{Pt-Pt} is 2.89 Å, which is only slightly longer than that observed in Pt metal (2.774 Å).[37] The inter-chain Pt–Pt distance is 9.89 Å. The intra-chain torsion angle of 45 ° minimizes steric hindrance between the cyanide ligands on adjacent $[Pt(CN)_4]^{1\cdot 7-}$ ions. The Br^- ions are located at the centre of the unit cell but only 60 % of the available crystallographic sites are occupied, and the 3-D random occupation of these sites leads to a random electostatic potential along the chain axis. The K^+ ions are located in one half of the unit cell whilst the water molecules occupy the other half. The water molecules form a hydrogen-bonded network between the cyanide ligands and either the bromide ion at the centre of the unit cell or the cyanide group of a $[Pt(CN)_4]^{1\cdot 7-}$ ion in an adjacent chain. Classical structural studies reveal that except for a progressive reduction in the unit-cell dimensions there is no marked change in the structure of KCP(Br) on cooling to 31 K.[36] ESCA and Mössbauer measurements down to low temperatures[14] have confirmed the electronic equivalence of the Pt atoms in the chain and therefore KCP(Br) belongs to class IIIb of Robin and Day's classification of mixed-valence compounds.[38]

The nature and temperature dependence of the PD in KCP(Br) has been investigated extensively by DXS[26] and elastic neutron scattering experiments.[39-41]

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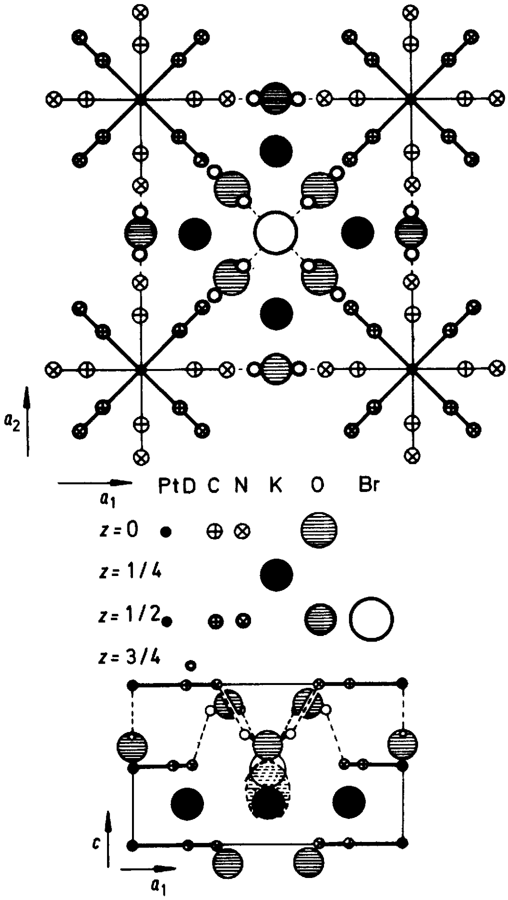

Figure 4 *Crystal structure of* KCP(Br). *Upper-projection along the conducting* c-*axis; lower-projection along one of the* a-*axes*
(Reproduced by permission from *Phys. Rep.*, 1978, **40**, 204)

DXS at room temperature showed that the PD was incommensurate with the basic lattice and had a repeat distance of $6.67d_{\mathrm{Pt-Pt}}$, in complete agreement with the Peierls period calculated from the DPO determined by chemical analysis. The diffuse lines observed at room temperature indicated that there was little correlation between the distortions on adjacent chains, whereas by 77 K the change from a diffuse line to broad spots indicated that the PD/CDW had become partially ordered in three dimensions. Elastic neutron scattering experiments have indicated that at 80 K the correlation length along the chains is over 100 Pt atoms, whereas the inter-chain correlation length is only about 5 inter-chain spacings.[40] It has been suggested that the 3-D ordering is incomplete because of the random occupation of the Br^- sites.[10] Neutron scattering studies have revealed that both static and dynamic distortions can be identified at room temperature and that the partial 3-D ordering occurs at $T_{3D} = 100\,K$.[39] It is not the Pt atoms alone, but the entire $[Pt(CN)_4]^{1.7-}$ ions that are displaced from their undistorted positions by the PD/CDW. However, the amplitude of the sinusoidal distortion is only 0.025 Å at 80 K.[40] [41]

The temperature dependence of the conductivity of KCP(Br) has been studied by Zeller and Beck[42] (Figure 5) and by Shchegolev and co-workers.[43] At about room temperature $\sigma_{\parallel}$ is 300 $\Omega^{-1}\,cm^{-1}$, the dependence of conductivity with temperature is slightly negative, and the degree of anisotropy $\sigma_{\parallel}/\sigma_{\perp}$ is about 10^5. Thus the electrical conduction behaviour at about room temperature is compatible with KCP(Br) being described as a 1-D metal. On lowering the temperature the conductivity passes through a maximum and the temperature dependence then becomes positive at lower temperatures. However, the behaviour in this region does not obey the linear relationship between $\ln \sigma_{\parallel}$ and inverse temperature which is found in a classical semiconductor. The first partial derivative of $\ln \sigma$, with respect to $1/T$, has a maximum at ~100 K corresponding to the partial 3-D ordering temperature T_{3D} found from neutron diffraction studies.[44,45] The conductivity also becomes frequency-dependent below T_{3D}. At somewhat lower temperatures KCP(Br) does behave as a semiconductor with a well defined band gap. Studies of the electrical conductivity of KCP(Br) under pressure indicate that T_{3D} increases and T_P decreases with increasing pressure, suggesting that the PD might be suppressed at pressures greater than 70 kbar.[45]

(ii) *Anhydrous AD Tetracyanoplatinate Salts.* A range of anhydrous AD tetracyanoplatinate salts containing Cl^- {*e.g.* $Cs_2[Pt(CN)_4]Cl_{0.3}$}, FHF^- {*e.g.* $Rb_2[Pt(CN)_4](FHF)_{0.4}$}, or F^- {*e.g.* $Cs_2[Pt(CN)_4]F_{0.19}$} as the anion[12,46,47] has been prepared. The structure of a typical example, $Rb_2[Pt(CN)_4](FHF)_{0.4}$, consists of a linear stack of square-co-planar $[Pt(CN)_4]^{1.6-}$ ions in which d_{Pt-Pt} is 2.798(1) Å and the torsion angle between adjacent $[Pt(CN)_4]^{1.6-}$ ions is 41.7(5)°.[47] This is the shortest d_{Pt-Pt} observed for a partially oxidized metal complex. Unlike KCP(Br), the cations in this structure are located in the same plane as the $[Pt(CN)_4]^{1.6-}$ ions. This maximizes the $M^+ \cdots N{\equiv}\bar{C}$ Coulombic interactions which are important for stabilizing the crystal lattice in the absence of any water of hydration. The FHF^- ions are aligned along the *c*-axis of the unit cell with a random occupation of possible sites and without correlation of the triatomic FHF^- ions in sites between neighbouring chains.

The structural features of the AD compounds indicate that d_{Pt-Pt} increases with (i) the size of the cation, (ii) the degree of hydration, and (iii) the size of the

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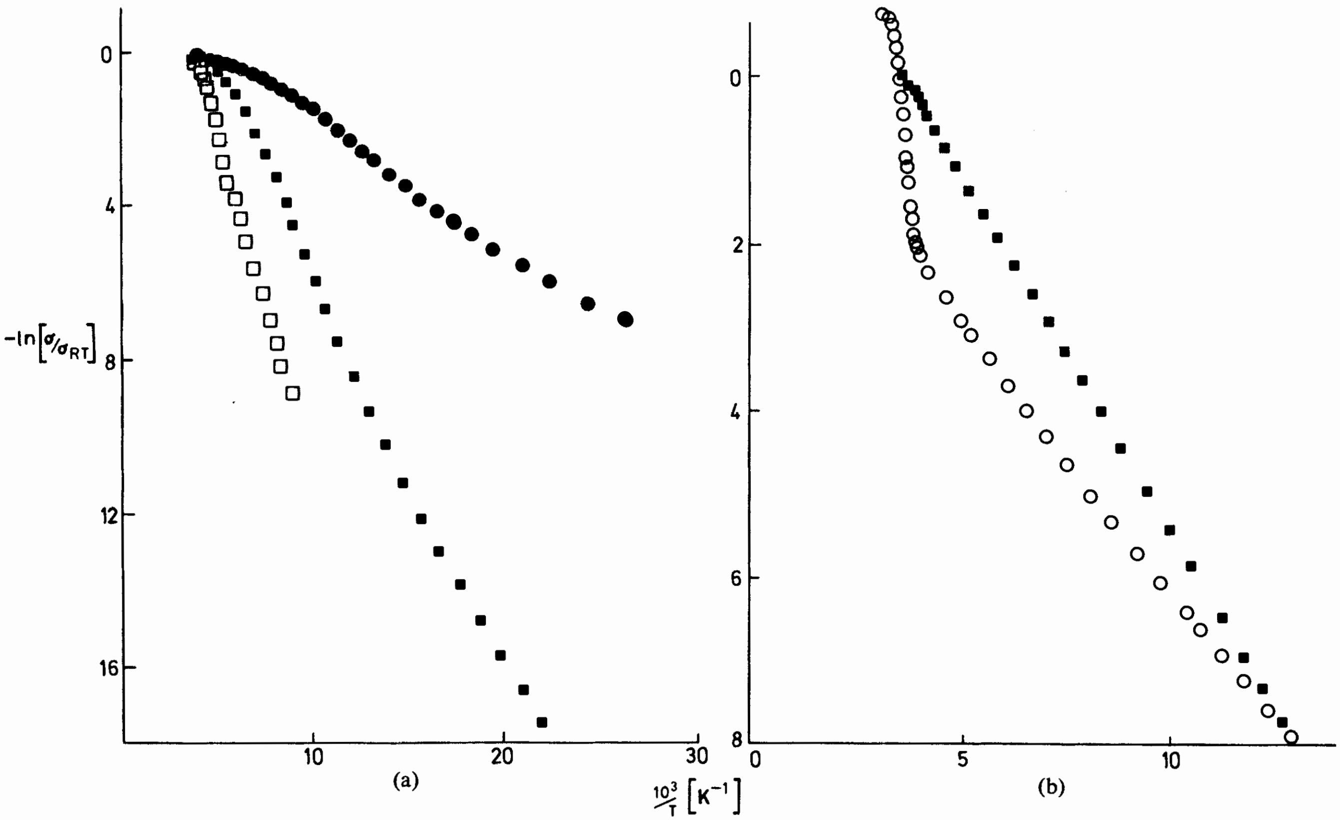

Figure 5 *Temperature dependence of* $\sigma_{\parallel}$ *for* (*a*) □ □ □ ACP(Cl), ■ ■ ■ KCP(Br), ● ● ● RbCP(FHF); (*b*), ■ ■ ■ Mg–OP, ○ ○ ○ Co–OP

excess anion. There is also an approximately linear relationship between the DPO and $d_{\mathrm{Pt-Pt}}$.[48] As might be expected, it also appears that $\sigma_{\parallel}$ is dependent on $d_{\mathrm{Pt-Pt}}$ with the highest conductivities being found for those compounds with the shortest $d_{\mathrm{Pt-Pt}}$ (see Table). A study of eight AD salts showed that the activation energy in the semiconducting region (and therefore the band gap) increases as $d_{\mathrm{Pt-Pt}}$ increases.[31] Other important solid-state parameters, *e.g.* λ, ϵ_F, and T_p, were also shown to be dependent on the DPO and $d_{\mathrm{Pt-Pt}}$.[31]

T_{3D} was found to decrease with decreasing $d_{\mathrm{Pt-Pt}}$.[31] In these compounds, 3-D ordering is likely to be a consequence of the static Coulombic coupling of the CDWs which will be susceptible to the presence of hydrogen bonding between the chains and influenced by the positions, size, and polarizability of the anions and cations in the lattice. Thus, the highest value of T_{3D} is found for ACP(Cl)[30] in which NH_4^+ ions can take part in additional hydrogen-bonding interactions not present in metal-cation salts. Similarly the lowest values of T_{3D} are found in the anhydrous compounds where there are few or no hydrogen-bonding interactions.

B. Cation-deficient Salts.—Cation-deficient 1-D metallic complexes are found for platinum with cyanide or oxalate as ligands. Over the past five years a number of studies on selected platinum complexes have revealed that the structures and physical properties of the CD salts are often much more complicated than those of the AD type. In particular, temperature-dependent 3-D superstructures are characteristic of the CD but not of the AD salts. The superstructure repeat distance in the platinum-atom chain direction can be either (a) the same as the PD{*e.g.* $Rb_{1.67}[Pt(C_2O_4)_2]\cdot 1.5H_2O$},[49] (b) a simple multiple of the PD{*e.g.* K(def)CP[50] and $Co_{0.83}[Pt(C_2O_4)_2]\cdot 6H_2O$},[27,51] or (c) not a simple multiple of the PD{*e.g.* $Mg_{0.82}[Pt(C_2O_4)_2\cdot 6H_2O$}.[27,52] These periodicities in the latter two cases have been termed Non-Peierls (NP) superstructures[51] because they give rise to distinct spots in *X*-ray experiments and not to the diffuse lines or modulated streaks characteristic of the PD/CDW.

(i) *CD Tetracyanoplatinate Salts.* The optical properties of a series of compounds of general formula $M_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$ (where M = K^+, Rb^+, or Cs^+) characterize these salts as 1-D metals.[33] Only the potassium salt, K(def)CP, has been studied in detail. The DPO for this salt is 0.25 and therefore the PD will have a repeat distance of 8 × $d_{\mathrm{Pt-Pt}}$ and this would be expected to lead to a crystal structure with an eight-fold superlattice repeat distance. Both *X*-ray[53] and neutron diffraction studies[50] at room temperature reveal that the unit cell contains four $[Pt(CN)_4]^{1\cdot 75-}$ ions stacked along the triclinic *c*-axis of the unit

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cell. The most significant feature of the structure is a zig-zag Pt-atom chain with a Pt(1)–Pt(2)–Pt(3) bond angle of 173.25(3)°. The Pt(2) atom is displaced perpendicular to the *c*-axis by 0.170(1)Å. The two crystallographically independent intra-chain platinum–platinum distances are of essentially equivalent length [2.961(1) and 2.965(1)Å] although the torsion angles between adjacent $[Pt(CN)_4]^{1\cdot75-}$ groups are all significantly different from 45°.[50] Unlike the hydrated AD tetracyanoplatinate salts, the water molecules in the CD salts hydrogen bond between cyanide ligands on adjacent $[Pt(CN)_4]^{1\cdot75-}$ anions in the same chain as well as taking part in inter-chain hydrogen bonding. The principal cause of the zig-zag Pt-atom chain is the asymmetrical environment about Pt(2) comprising mainly H_2O molecules on one side and K^+ ions on the other. Kobayashi *et al.*[54] have shown that below about 294K a transition occurs to give a new unit cell (*a*, 2*b*, 2*c*) in which the repeat distance along the *c*-axis is the same as the period of the PD/CDW. The temperature dependence of $\sigma_{\parallel}$ in K(def)CP is well established but the interpretation of the behaviour has been the subject of controversy and conflicting explanations.[55] [56] However, the evidence from these and other measurements suggests a NP transition at ~300K and a Peierls transition at $T_{3D} \approx 50K$.[15]

(ii) $Rb_{1.67}[Pt(C_2O_4)_2]\cdot1.5H_2O$, (Rb–OP). In Rb–OP the DPO is a simple fraction (1/6) and therefore the PD can be determined with precision from classical structural analysis. Kobayashi *et al.*[49] showed that Rb–OP contains a distorted non-linear six-fold Pt-atom chain with very dissimilar intra-chain Pt–Pt separations of 2.717(3), 2.830(3), and 3.015(3)Å. Rb–OP has a very low value for $\sigma_{\parallel}$ at room temperature ($10^{-3}\,\Omega^{-1}\,cm^{-1}$)[49] compared with the other 1-D metallic complexes that have been studied. This can be readily understood in terms of the one long intra-chain Pt–Pt separation of 3.015(3)Å which is only slightly shorter that that found in some semiconducting integral oxidation state tetracyanoplatinate(II) salts.[17] Rb–OP behaves as a semiconductor between 305 and 83K with an activation energy of 0.077 eV and with no evidence of metallic behaviour.

(iii) *Divalent CD bis(Oxalato)platinate Salts.* A series of CD bis(oxalato)platinate salts $M_{0.8}[Pt(C_2O_4)_2]\cdot6H_2O$ (where M = Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, or Zn^{2+})[23,24,34,57] which are isostructural at room temperature have been studied. The cobalt salt (Co–OP) contains linear chains of $[Pt(C_2O_4)_2]^{1\cdot66-}$ ions with equidistant Pt–Pt intra-chain separations of 2.841Å and torsion angles of 55° between adjacent complex anions along the chains (Figure 6).[23] The divalent metal ions are located between the planes containing the $[Pt(C_2O_4)_2]^{1\cdot66-}$ ions and co-ordinated to six water molecules with a slightly distorted octahedral geometry. There are eight crystallographic sites for the divalent metal ions per unit cell and 41% of these sites are randomly occupied in 3-D. The chains of $[Pt(C_2O_4)_2]^{1\cdot66-}$ ions are cross-linked by a hydrogen-bonded network of water molecules which are located in the planes containing the anions.

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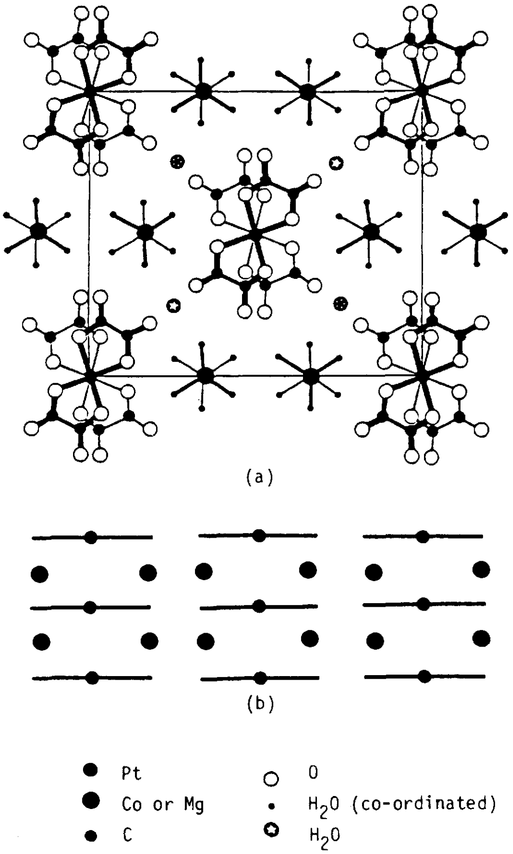

Figure 6 *Crystal structure of* Co–OP: (a), *projection parallel to* Pt-*atom chains;* (b), *projection perpendicular to* Pt-*atom chains*
(Reproduced by permission from 'Molecular Metals' ed W. E. Hatfield, NATO Conference Series: VI, Materials Science, Plenum Press, New York, 1979, Vol. 1, p. 378)

Braude *et al.*[51] have shown that above 304K Co–OP is modulated only by the 1-D PD. However, below this temperature a 3-D superlattice begins to develop and is fully formed by 250K. From the relative positions of the diffuse lines arising from the PD and the spots due to the 3-D superlattice it was found that the NP superlattice had a periodicity in the chain direction of twice that of the PD. The temperature dependence of the intensity of the diffuse lines due to the PD, and the spots due to the NP superlattice, indicates that T_{3D} and the transition temperature for the NP superlattice, T_{NP}, are close together. This results in Co–OP undergoing two simultaneous transitions which appear to be coupled together.[51] The electrical conduction properties of Co–OP can be explained in terms of the structural changes described above. Both the d.c. conductivity[58] and the conductivity measured at 35 GHz[59] ($\sigma_{\parallel} = \sim 20\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at room temperature) decrease abruptly between room temperature and 250 K where a sharp transition occurs to a low-temperature regime which has a much smaller activation energy of 0.05—0.06 eV (Figure 5). Above 250 K the conductivity is frequency-independent, but below this temperature where the PD and the 3-D superstructures are fully developed the conductivity varies with frequency.[59]

DXS experiments at room temperature on $Ni_{0.84}[Pt(C_2O_4)_2]\cdot 6H_2O$, (Ni–OP), and Zn–OP reveal, as for Co–OP, partially formed 3-D superstructures where the period of the superstructure in the platinum-atom chain direction is twice that of the PD.[27] Ni–OP[24] and Zn–OP[34] also exhibit a very similar temperature dependence of conductivity to that observed in Co–OP.

In $Mg_{0.82}[Pt(C_2O_4)_2]\cdot 6H_2O$, (Mg–OP), the platinum-atom chains are modulated by only the PD at temperatures above 283—285 K, but in this temperature range the salt undergoes a phase change with the concomitant formation of a 3-D superstructure.[52] The periodicity of this NP superlattice in the platinum-atom chain direction is not a simple multiple of the PD. Moreover, diffuse *X*-ray scattering experiments show that 3-D ordering of the Peierls distorted chains does not occur at temperatures > 97 K.[52] The temperature dependence of the conductivity of Mg–OP[58] is very different from that of Co–OP, Ni–OP, or Zn–OP with an approximately linear dependence of $\ln \sigma_{\parallel}$ upon inverse temperature between 298 and 40 K and with an activation energy of $\sim$0.07 eV. There are no major changes in $\sigma_{\parallel}$ on passing through the phase change although there is a minimum in the thermopower at this temperature.[24] There is no evidence from DXS experiments for a 3-D superstructure in $Mn_{0.81}[Pt(C_2O_4)_2]\cdot 6H_2O$, (Mn–OP), at room temperature.[27]

The important role of the cation in the lattice upon the physical properties of the CD bis(oxalato)platinate salts is clearly illustrated by the two strikingly different types of temperature dependence of conductivity observed for (a) Co–OP, Ni–OP, and Zn–OP and (b) Mg–OP. These differences have been rationalized[24] in terms of the polarizing power of the cation which follows the order $Zn^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Mg^{2+}$. The presence of the cations having the higher polarizing powers, *e.g.* Co^{2+}, Ni^{2+}, or Zn^{2+}, results in increased polarization of the hydrogen-bonded network of water molecules and hence increased inter-chain coupling. This leads to a relatively high value of T_{3D} which is then comparable to T_{NP} and the two types of lattice distortion couple together. The coupling together of the NP and PD superstructures appears to be responsible for the sharp decrease in conductivity between room temperature and 250 K observed in Co–OP, Ni–OP, and Zn–OP. In the presence of cations with smaller polarizing powers, *e.g.* Mg^{2+}, the water molecules are polarized to a smaller degree and T_{3D} is relatively low. In this case, since T_{3D} and T_{NP} are dissimilar, there is no coupling together of the PD and the NP superlattice. This explains

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[59] H. J. Pedersen and A. E. Underhill, *Solid State Commun.*, 1980, **33**, 289.

why no sharp transition is observed in the temperature dependence of $\sigma_{\parallel}$ for Mg–OP (Figure 5).

5 General Discussion and Outlook

Over the past few years chemists have succeeded in synthesizing many new partially oxidized tetracyanoplatinate and bis(oxalato)platinate salts. This work has resulted in a series of both hydrated and anhydrous AD tetracyanoplatinate salts and a number of hydrated CD tetracyanoplatinate salts. However, only hydrated CD bis(oxalato)platinate salts have been reported. As discussed in Section 4, relatively small chemical modifications can have a very profound effect on the solid-state properties of these complexes. These effects are often complicated, but it has been established that where the NP superstructure is commensurate either with the underlying lattice [*e.g.* K(def)CP or Rb–OP] or with the PD/CDW (*e.g.* Co–OP) there is a significant reduction in $\sigma_{\parallel}$ compared with compounds in which the NP superstructure is either absent (*e.g.* Mn–OP) or incommensurate (*e.g.* Mg–OP) with the other two periodicities. The influence of hydrogen-bonding interactions and the polarizing power of the cations upon T_{3D} and η demonstrates how the coupling between the metal-atom chains is sensitive to subtle changes in the crystal lattice. These relationships point the way to the synthesis of new compounds which have higher electrical conductivities and retain their metallic properties to lower temperatures. Many attempts have been made to produce more radical changes in properties by synthesizing 1-D metallic complexes with metals other than platinum, or ligands other than cyanide or oxalate. Few of these attempted syntheses have been successful, but preliminary results suggest that partially oxidized bis(squarato)platinate salts {*e.g.* $K_{1.6}[Pt(C_4O_4)_2]\cdot 2H_2O$} are new 1-D metals.[60]

The application of 1-D metallic complexes may be limited by the brittle nature of the crystals and by the ease with which the hydrated compounds lose water. Nevertheless the strong dependence of $\sigma_{\parallel}$ upon the ambient humidity[61] in KCP(Br) suggests its possible use as a humidity sensor. Moreover, the highly anisotropic optical properties of the anhydrous compounds could be used to produce polarized i.r. radiation. The greatest potential application of 1-D metals centres on their possible development as high-temperature superconductors. Little has suggested that a partially oxidized chain of platinum atoms could form the conducting spine in an excitonic superconductor.[62] It might also be possible to realise very high conductivities by the Fröhlich mechanism in 1-D metallic complexes (Section 3).

The last decade has seen a large increase in the variety of 1-D metallic complexes available for study and a much better understanding of the relationship between the composition, structure, and solid-state properties of this class of compounds. However, much remains to be done before these systems are fully

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[62] D. Davis, H. Gutfreund, and W. A. Little, *Phys. Rev. (B)*, 1976, **13**, 4766.

understood and before compounds having a predetermined combination of solid-state properties can be synthesized.

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