The Platinum Metals in Quasi One-Dimensional Solids

NOVEL MATERIALS WITH A POTENTIAL FOR NEW SOLID STATE TECHNOLOGY

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The platinum metals feature distinctly in a class of highly anisotropic compounds exhibiting one-dimensional properties. An understanding of their molecular structure and their physical and electronic properties permits the synthesis of anisotropic insulators, semiconductors and metals. The possibility of room temperature superconductivity continues to be a focal point of current research.

In the past ten years considerable interest has arisen in the chemical and physical properties of highly anisotropic quasi one-dimensional (Q1–D) solids. These include organic, inorganic and organo-metallic compounds whose properties such as electrical conductivity, optical absorption and tensile strength are much larger in one direction in the solid than in any other. Detailed studies have revealed also the occurrence of physical phenomena peculiar to limited dimensionality systems including electronic excitations which may form a basis for new technology. In understanding the relationship between physical properties and molecular bonding and structure it will be possible to engineer well-defined compounds exhibiting specific properties.

Within this class of compounds mixed valence chemistry and metal atom chain complexes form an important part. This includes integral and non-integral oxidation state metal complexes with columnar structures. Tetra co-ordinated metal plane complexes have featured strongly in this field where the central metal atoms with d^1 and d^8 electronic configurations allow columnar structure formation having the desired chemical and physical properties. Rh^I, Ir^I, Pd^{II} and Pt^{II} satisfy the d^8 requirements and are consequently receiving increasing attention. The latter particularly, has been studied extensively and forms the basis of the most well-known tetracyano platinate $K_2[Pt(CH)_4]$-$Br_{0.3}.3H_2O$ which behaves as a one-dimensional metal at room temperature.

Electron Band Theory

The physical properties of a solid depend on the electronic structure and interatomic interactions of the atoms that form it. When the electron-site interaction is strong and atoms, or molecules, are brought into contact, so that their orbitals overlap, tight-binding band theory predicts that the allowed electron energy states of the isolated molecules spread out, in energy, to form a band of states for each molecular orbital. The band-widths are directly related to the degree of orbital overlap and respective bands are separated from each other by energy gaps in which electron states cannot exist, as illustrated in Figure 1. In an insulator the highest band (conduction band) is empty whereas the next lowest band (valence band) is completely full and the energy gap between them is large, usually 2 eV or more. In a semiconductor the energy gap is smaller and electrons in response to an
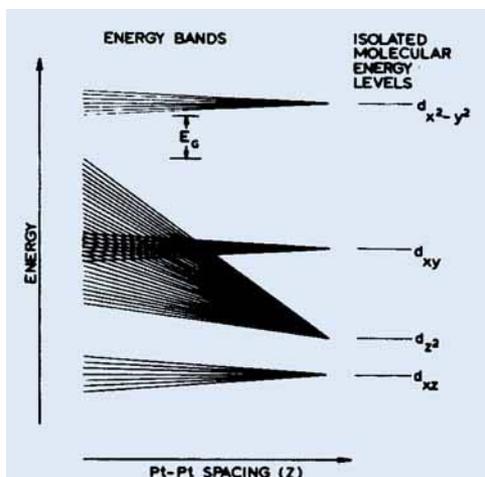
Fig. 1   Electron energy band formation arising from the overlap of isolated site molecular orbitals as the sites approach each other to form a solid. This is schematically shown for two $Pt(CN)_4^{2-}$ ions (4)

applied electric field may gain energy and move to the conduction band constituting a current flow. If the outer electron orbitals are incompletely filled a partly filled band will result in which electrons can readily occupy higher energy states within the same band resulting in metallic behaviour. In usual insulators, semiconductors and metals, the electronic response is almost independent of direction whereas in Q1–D solids enhanced electronic response occurs in only one direction.

Columnar Metal Chain Structure and Properties

Many reviews have appeared on the physics and chemistry of inorganic and organometallic Q1–D systems. These include those by Krogman (1), Thomas and Underhill (2), Zeller (3) and Miller and Epstein (4). Short reviews may also be found in two books devoted to Q1–D solids (5, 6). Within the existing framework of classification it is constructive to consider integral oxidation state compounds exhibiting insulating and semi-

conducting properties and non-integral oxidation state compounds with varied properties, including metallic.

Integral Oxidation State Complexes

To form a metal atom chain columnar structure of the type illustrated in Figure 2, a co-planar monomer complex is required. Four co-ordinate square complexes including a central metal ion with d^8 electronic configuration, such as Rh^I, Ir^I, Pd^{II} and Pt^{II}, may be used. The metal atom 4d or 5d electrons extend to neighbouring monomers allowing orbital overlap whereby electron delocalisation along the metal atom chain occurs. Thus there exists a potentially conducting chain surrounded by insulating ligands. The latter act to separate columns and monomer-monomer inter-ligand interactions usually lead to a staggered plane configuration. They also affect the metal atom chain electronic states.

If z is the stacking direction the p_z and d_{z^2} metal atom orbitals overlap. If the latter are fully occupied a filled d_{z^2} band results. Recent considerations have shown that the next highest unfilled band is the $d_{x^2-y^2}$ or p_z band depending on metal ion and metal-metal separation. The energy gap is also dependent on metal ion separation and an insulator or semiconductor is expected.

Some anion chain tetracyano complexes of palladium and platinum may be compared as in Table I, showing that the chain repeat unit

Table I
Crystallographic chain repeat units for some platinum and palladium tetracyano complexes. (See A. E. Underhill in (5))

Compound	Symmetry	C(Å)
$BaPt(CN)_4.4H_2O$	Monoclinic	6.54
$BaPd(CN)_4.4H_2O$	Monoclinic	6.73
$CaPt(CN)_4.5H_2O$	Orthorhombic	6.72
$CaPd(CN)_4.5H_2O$	Orthorhombic	6.84

Table II
Metal-metal separation and chain d.c. conductivity of some platinum tetracyano complexes. (See A. E. Underhill in (5))

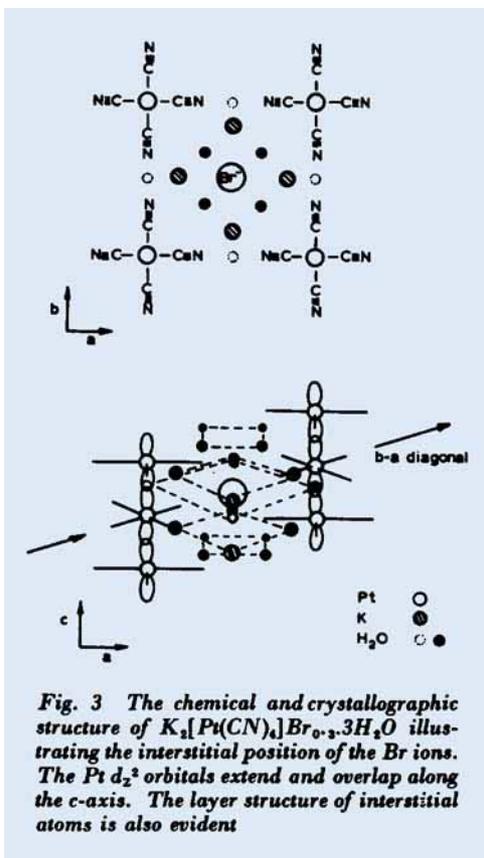| Compound	Pt–Pt (Å)	$\sigma_{\parallel}(\Omega^{-1}cm^{-1})$
$BaPt(CN)_4.4H_2O$	3.27–3.32	$8–50 \times 10^{-7}$
$K_2Pt(CN)_4.3H_2O$	3.5	$5–10 \times 10^{-8}$
$Li_2Pt(CN)_4.nH_2O$	3.18	$4–30 \times 10^{-4}$

is smaller in the platinum complexes. This is considered a result of the larger 5d orbitals in platinum compared to the 4d in palladium. Table II illustrates the situation for three cyanoplatinates where the conductivity, measured parallel to the chain direction (σ), increases with decreasing metal-metal separation. For neutral chain complexes the results are similar, as shown in Table III for the iridium and rhodium dicarbonylacetylacenato complexes,

(where R is $CH_3 — C — CH = C — CH_3$)
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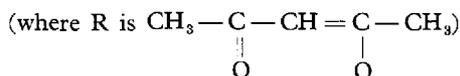
As with palladium and platinum, the metal–metal separation is less in iridium than in rhodium, giving a higher conductivity with a correspondingly low activation energy. Large organic ligand groups cause an increase in metal separation due to mutual complex repulsion, so small ligands are preferable. Regarding optical absorption, increasing metal-metal interaction results in red-shifted

Fig. 2 Typical metal atom chain columnar structure formed by metal atom (M) interaction along the z-axis and involving d_{z^2} orbital overlap. Steric restraints and interligand repulsion stagger the ligands (L) and restrict metal atom approach. The ligands also act to separate adjacent chains

Table III
Metal-metal separation, chain d.c. conductivity, conductivity anisotropy and activation energy for an iridium and rhodium dicarbonylacetylacenato complex (2, 5)

Compound	M–M(Å)	$\sigma_{\parallel}(\Omega^{-1}cm^{-1})$	$\sigma_{\parallel}\sigma_{\perp}$	$\Delta E(eV)$
$Rh(CO)_2R$	3.26	10^{-11}	>100	0.32–0.44
$Ir(CO)_2R$	3.21	10^{-5}	>500	0.25–0.27

Fig. 3 The chemical and crystallographic structure of $K_2[Pt(CN)_4]Br_{0.3}.3H_2O$ illustrating the interstitial position of the Br ions. The Pt d_{z^2} orbitals extend and overlap along the c-axis. The layer structure of interstitial atoms is also evident

(lower E_g) absorption and complexes containing electron accepting ligands also exhibit a lower E_g, absorb strongly in the red and appear deep blue or violet.

Thus an opportune choice of integral oxidation state metal atom and ligand system may give anisotropic semiconductors with chain conductivities in the range 10^{-2} to 10^{-12} $\Omega^{-1}cm^{-1}$, activation energies from 0.1 to 2eV and anisotropies of larger than 500 in conductivity.

Highly Conducting and Non-Integral Oxidation State Complexes

Two principal routes are available to form highly conducting and metallic Q1–D solids of the platinum metals:

(a) Decrease the d_{z^2}–$d_{x^2-y^2}$ (or p_z) band

gap using strongly electron accepting ligands.

(b) Partially oxidise the chain metal atoms so the filled d_{z^2} band is depopulated giving an incompletely filled metallic band.

Option (a) leads to semiconducting behaviour and the complex may visually appear metallic. This case may apply to the carbonyl chloride iridinate $Ir(CO)_3Cl$ the stoichiometric structure of which has recently been confirmed by Reis et al (7). This compound is also unusual in that there are two crystallographically inequivalent iridium sites which subtend an angle of 178.5° between them along the chain, and neighbouring monomer units are staggered with a stacking disorder resulting in close overlap of one Cl and one CO ligand. The column is weakly helical. An Ir-Ir separation of 2.84Å is found with a room temperature $\sigma_{||}$ of 0.2 $\Omega^{-1}cm^{-1}$ and the complex has a metallic lustre. However, the behaviour is unclear and metallic properties cannot be considered established.

The most extensively studied Q1–D non-integral oxidation state complex is KCP(Br) ($K_2[Pt(CN)_4]Br_{0.3}.3H_2O$), shown in Figure 3, and the analogous chloride. As we saw earlier $K_2Pt(CN)_4$ is at best a wide band gap semiconductor where the two d_{z^2} electrons produce a filled band. In KCP(Br) the interstitial bromine atoms act as strong electron acceptors which subtract on average 0.3 electrons from each $Pt(CN)_4$ group causing the d_{z^2} band to be about 5/6 full and hence metallic. The Pt-Pt separation is 2.89Å. Its room temperature conductivity is about 300 $\Omega^{-1}cm^{-1}$ parallel to the chain and about 10^5 times smaller perpendicular to it. Also KCP(Br) exhibits striking metallic reflectance for light polarised parallel to the chain direction, resembling closely the Drude behaviour for free electrons, whereas perpendicular to the chains it is typical of an insulator (3, 6).

However, the stability of this metallic state at lower temperatures is threatened by the very properties that produced it, namely the

one-dimensional array and the interaction of electrons within it. Below 270K $\sigma_{\parallel}$ and $\sigma_{\perp}$ decrease with decreasing temperature. Below 100K they decrease very rapidly as shown in Figure 4. What accounts for this behaviour?

Physics in One-Dimension

As predicted independently by Fröhlich (8) and Peierls (9) a one-dimensional metal at 0K is inherently unstable against a lattice distortion which doubles the size of the chain repeat unit. The static distortion introduces an energy gap across the conduction band by displacing occupied states to lower energy and raising the empty ones resulting in a net reduction of energy. The system is more stable after the transition but it is now insulating or semiconducting. However, the Peierls-Fröhlich (P-F) (or metal-insulator) transition arises dynamically through the interaction of electrons and phonons and Kohn pointed out (10) that a strong inter-action results in a reduction in the energy of the phonon whose wavelength corresponds to that of the new periodic distortion. The Kohn anomaly has been observed in KCP(Br) using neutron scattering. A doubling of the chain repeat unit is observed below 100K by X-ray diffraction and is accompanied by the formation of an energy gap which is zero at the transition temperature and increases to a fixed value at 0K. This explains the con-ductivity behaviour below 100K. Stabilisation of a Q1-D metal by averting a P-F transition could be achieved by:

(a) Large ligands impeding the lattice dis-tortion.
(b) Introducing three-dimensional char-acter to make the transition less ener-getically favourable.
(c) Controllably introducing a degree of chain periodicity disorder. The latter may occur unintentionally and be of great use.

However, the new P-F lattice periodicity produces a periodic potential leading to a periodic variation in electron density referred to as a charge density wave (CDW). The
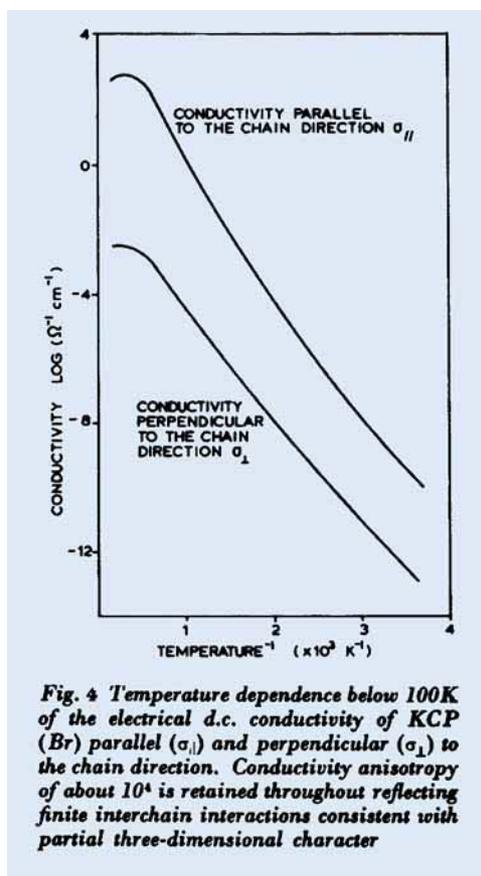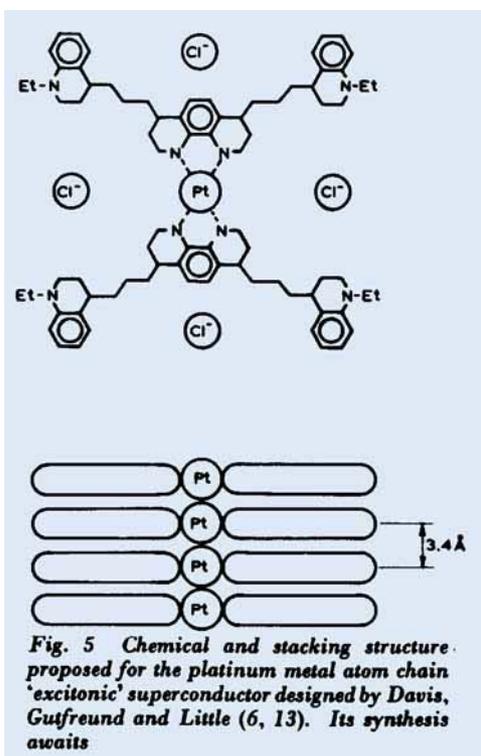

Fig. 4 *Temperature dependence below 100K of the electrical d.c. conductivity of KCP (Br) parallel ($\sigma_{\parallel}$) and perpendicular ($\sigma_{\perp}$) to the chain direction. Conductivity anisotropy of about 10^4 is retained throughout reflecting finite interchain interactions consistent with partial three-dimensional character*

CDW and lattice distortion form self-con-sistently and in combination form a con-densate. The important point is that the CDW condensate, under the influence of an electric field, may move unattenuated along the chain giving rise to a very high conduc-tivity or Fröhlich superconductivity (pseudo superconductivity exhibiting no Meissner effect). However, real systems contain defects which will pin the condensate reducing the conductivity. Pinning of the CDW may explain the conductivity behaviour of KCP-(Br) above 100K. Indeed, the low tempera-ture far infrared reflectivity exhibits a peak at 15 cm^{-1} commensurate with a pinned oscillating CDW (5, 11).

True superconductivity with the attraction of transition temperatures at or above room temperature has been a serious goal for

Fig. 5 Chemical and stacking structure proposed for the platinum metal atom chain 'excitonic' superconductor designed by Davis, Gutfreund and Little (6, 13). Its synthesis awaits

conductor based on a platinum atom chain surrounded by a co-ordinated sheath of highly polarisable phenanthroline dye ligands as shown in Figure 5. The dye ligands act as "exciton" sites mediating the interaction of electrons along the metal atom chain. This choice was probably influenced by KCP(Br) but in the superconductor complex the large Pt-Pt separation of 3.4Å may prohibitively limit the bandgap and bandwidth requirements for super-conductivity assuming of course that the complex can be synthesised.

It is clear that many of the current and anticipated properties of Q1–D complexes could have great technological appeal particularly in the semiconductor and solid state device industry. Electronic and optical property design capability exists with the uniqueness of intrinsic anisotropy and the potential of single molecular chain communication providing up to 10^{14} physical channels per cm². Room temperature superconductivity, if achieved, may not be immediately useful for high power transmission but in device applications requiring small and electronically fast solids, Q1–D compounds may excel. Realisation of these somewhat speculative prospects requires a more extensive understanding of chemical bonding and structure in these solids and the relationship with physical properties including material perfection. The platinum metals will continue to feature significantly in this most interesting field.

workers in Q1–D solids since the suggestion by Little (12) that effective attraction between electrons could be achieved by an exchange of an electronic excitation (or "exciton") rather than phonons as in the BCS theory. This idea has recently been revived by Davis, Gutfreund and Little (6, 13) with the emergence of a new design of excitonic super-

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