

One-dimensional Metallic Conductors

A NEW CLASS OF PLATINUM COMPLEXES

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Certain partially oxidised transition metal complexes possess structural and electronic properties which suggest that they are capable of development as one-dimensional metallic conductors. Studies of such platinum complexes have proved the most encouraging and may lead to the development of high temperature superconductors.

There is, at present, a great interest in compounds possessing new and unique electronic properties, because the successful application of these compounds may lead to devices with as large an impact on technology as the silicon and germanium devices of the last two decades. One class of compound at present being studied in several laboratories throughout the world is that possessing structural and electronic properties which suggest the possibility of one-dimensional metallic conduction. Two main series of compounds which appear capable of development to give this type of behaviour are being investigated. One series consists of organic charge-transfer compounds containing the TCNQ (tetracyanoquinodimethane, see Fig. 1a) molecule and the other series contains some partially oxidised transition metal complexes. This article concerns the latter complexes which were briefly mentioned in a previous *Platinum Metals Review* article (1).

The transition metal complexes which appear to be capable of development as one-dimensional metallic conductors are those in which the metal atom is surrounded by a square-coplanar arrangement of ligands and in which the square-coplanar units are stacked above one another to form a chain of metal atoms running throughout the crystal (see Fig. 2). This type of complex is mainly limited to nickel(II), palladium(II), and

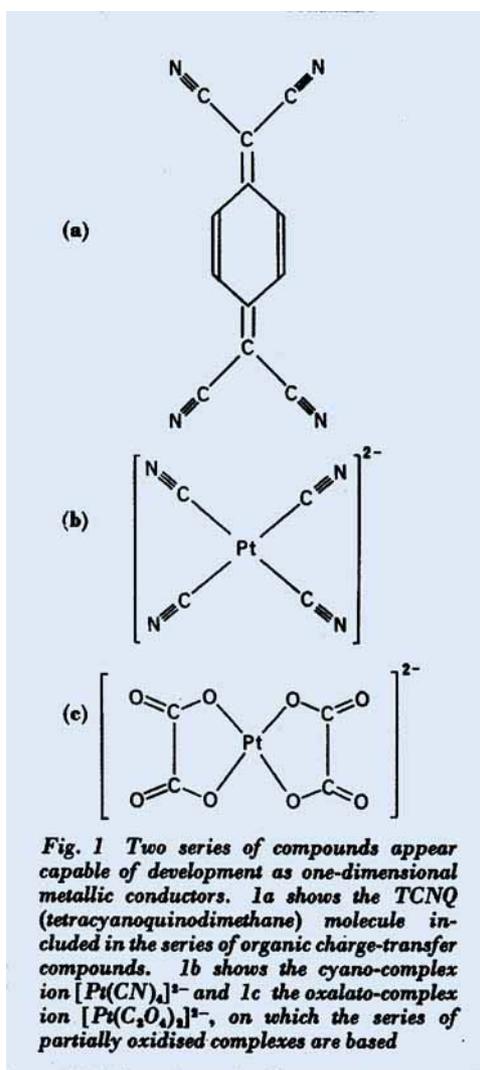


Fig. 1 Two series of compounds appear capable of development as one-dimensional metallic conductors. 1a shows the TCNQ (tetracyanoquinodimethane) molecule included in the series of organic charge-transfer compounds. 1b shows the cyano-complex ion [Pt(CN)₄]²⁻ and 1c the oxalato-complex ion [Pt(C₂O₄)₂]²⁻, on which the series of partially oxidised complexes are based

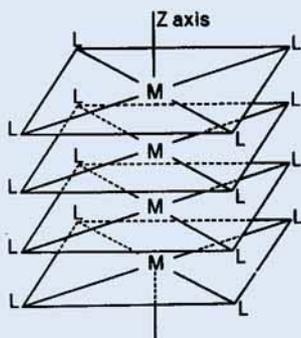


Fig. 2 Transition metal complexes capable of development as one-dimensional metallic conductors contain the metal atom *M* surrounded by a square-coplanar arrangement of ligands *L*. The square-coplanar units are stacked above one another to form a chain of metal atoms running through the crystal

platinum(II) compounds and these have been discussed in detail in a recent review (2). The electrical conduction properties of several examples of this type of complex have been studied (e.g. $\text{Ni}(\text{dmg})_2$ where *dmg* is dimethylglyoxime (3), $\text{Pt}(\text{NH}_3)_4 \cdot \text{PtCl}_4$ (4), and $\text{K}_2\text{Pt}(\text{CN})_4 \cdot x\text{H}_2\text{O}$ (5)) and they have been found to behave as semiconductors with the conductivity in the direction of the metal atom chain ($\sigma_{||}$) ranging from 10^{-4} to 10^{-10} $\text{ohm}^{-1}\text{cm}^{-1}$ at room temperature.

In this type of complex it has been suggested (2) that the outermost p_z and d_z^2

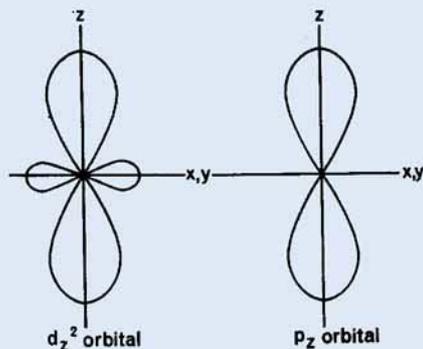
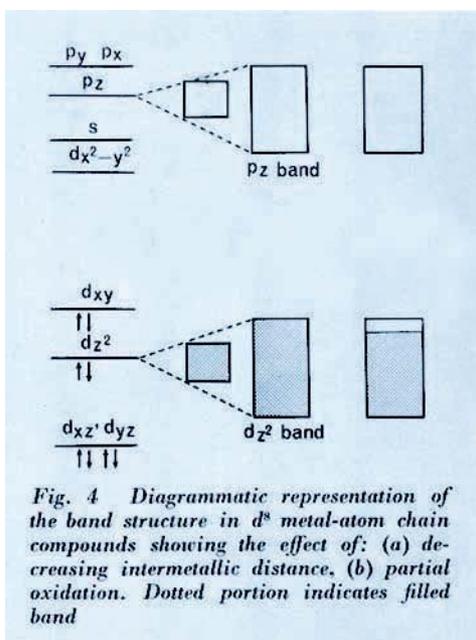


Fig. 3 Orbitals used in the formation of a band structure

orbitals (Fig. 3), or a combination of these orbitals, on adjacent metal atoms may overlap to form a d_z^2 band and, at higher energy, a p_z band. In the case of nickel(II), palladium(II) and platinum(II) complexes, each d_z^2 orbital contains two electrons, while the p_z orbital is empty, and therefore the d_z^2 band is completely full and the p_z band is completely empty (Fig. 4). The semi-conduction properties of these compounds can therefore be understood in terms of promotion of electrons from the filled d_z^2 band to the empty p_z band. Alternatively, the observed conductivity may result from electrons "hopping" from one square coplanar complex to the next one in the chain, the hopping process being thermally activated.

Metallic conduction is associated with an incompletely filled band, and several different types of complex having the general structure described above, and in which further partial oxidation (i.e. removal of electrons) of the central metal atom has occurred, have been characterised (6). In these compounds the d_z^2 band, if present, would be incompletely filled and hence be expected to confer metallic properties on the complex (See Fig. 4). Because the d_z^2 orbitals are directed along the *z* axis only, and not along the *x* or *y* axes, the resulting partly filled band will be confined to one axis of the crystal. Thus it is expected that the metallic properties of the crystal will exist in one dimension only and that the crystal will behave as a semiconductor along the other two axes.

There are two main types of partially oxidised complex. One type is based on the cyano-complex ion $[\text{Pt}(\text{CN})_4]^{2-}$ (see Fig. 1(b)) and the other on the oxalato-complex ion $[\text{Pt}(\text{C}_2\text{O}_4)_2]^{2-}$ (Fig. 1(c)). The small size of the ligand atoms and the multiple bonding characteristics of the cyanide and oxalate ligands appear to be important in the formation of partially oxidised systems. These partially oxidised complexes are at present almost exclusively restricted to platinum as the central metal. Platinum is the largest



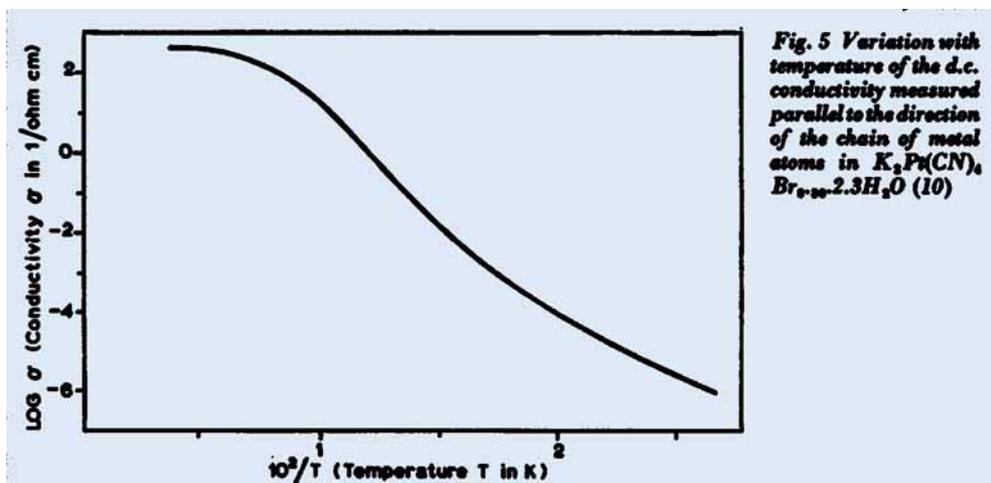
of the elements Ni, Pd and Pt, and therefore possesses the largest orbitals. This increases the chance of effective overlap with the orbitals of the adjacent metal atoms for a given intermetallic distance and thus facilitates the formation of a delocalised d_z^2 band. In these complexes partial oxidation of the platinum can be achieved by either incorporating excess anions into the lattice (e.g. $K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$) or by the creation of a deficiency of cations (e.g. $K_{1.74}Pt(CN)_4 \cdot 1.8H_2O$ or $Mg_{0.82}[Pt(C_2O_4)_2] \cdot 5.3H_2O$). The extent of oxidation of the platinum is always about 2.3–2.4.

Crystal Structure

The crystal structure of $K_2Pt(CN)_4Cl_{0.32} \cdot 2.6H_2O$ has been determined (7) and consists of square-coplanar $[Pt(CN)_4]^{1.7-}$ units stacked above one another along the c (needle)-axis of the crystal. Alternate units are staggered by 45° which reduces steric repulsion between the cyanide ligands. The Cl^- ions are in the centre of the unit cell surrounded by a tetrahedral arrangement of K^+ ions. However, only 64 per cent of the unit cells contain a Cl^- ion and this corresponds

to $0.32Cl^-$ per Pt atom and hence results in an oxidation number of 2.32 for the platinum. All the platinum atoms are crystallographically identical, indicating that the excess charge is delocalised along the metal atom chain. $K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$ possesses a similar structure (7). The effect of the partial oxidation is to bring the platinum atoms closer together. In the platinum(II) cyano-complexes the Pt-Pt distance is always $>3.1\text{\AA}$ whereas in the partially oxidised compounds it is only $2.8\text{--}2.9\text{\AA}$, which compares with 2.77\AA in platinum metal. Similar intermetallic distances have been found in the partially oxidised platinum oxalate-complexes.

The crystals of the partially oxidised compounds have a completely different appearance from their platinum(II) counterparts. Whereas the latter are either colourless or only weakly coloured, the partially oxidised compounds are a deep copper colour with a metallic reflection. The optical reflectivity spectrum has been determined (8) for $K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$ with light polarised either parallel or perpendicular to the direction of the platinum atom chains. For light polarised perpendicular to the chains the reflectivity is small and essentially independent of the wavelength. For light polarised parallel to the platinum atom chains the reflectivity is about 85 per cent at low energy and then falls sharply to almost zero at about $625m\mu$. The parallel polarised spectrum can be interpreted using the Drude theory of the optical behaviour of a metal and this indicates the presence of charge carriers that are highly mobile parallel to the platinum atom chains and localised perpendicular to them. From the optical spectrum the electrical conductivity in the direction of the platinum atom chain has been estimated as $10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$ and the carrier concentration as close to that of a metal (8). The visual appearance of the crystals persists down to 4 K, indicating that the metallic properties are still present at this temperature. The presence of a Pauli temperature-independent



paramagnetism has been detected in crystals of $K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$ and also has been interpreted as arising from the presence of free metallic electrons in this compound (9).

Conductivity

Although the optical properties and paramagnetism of crystals of $K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$ indicate a metallic state for electrons parallel to the c-axis of the crystal, the electrical conduction properties of these compounds are more complicated. The d.c. conductivity of these compounds has been extensively studied and conductivities as high as $10^9 \text{ ohm}^{-1} \text{ cm}^{-1}$ have been reported (10) at room temperature for single crystals in the direction of the platinum atom chains. The value of the conductivity and its variation with temperature varies, however, with the method of preparation, extent of dehydration etc. Single crystals are highly anisotropic conductors with $\sigma_{\parallel} : \sigma_{\perp} = 10^2 - 10^8$, indicating a much better conduction pathway parallel to the platinum atom chains than in the direction perpendicular to the chains, as expected from the crystal structure and optical properties. Although the conductivity is high at room temperature it falls with decreasing temperatures and below 200K the crystals are well-behaved semiconductors with a similar activation energy for conduction

parallel and perpendicular to the metal atom chains (see Fig. 5) (10, 11). Above 200K the activation energy decreases with increasing temperature and eventually at about room temperature the conductivity is almost temperature-independent. At higher temperatures there are indications that a negative temperature coefficient for conduction may occur, i.e. a so-called semiconductor-to-metal transition (10). This behaviour has been observed for several of these complexes and is particularly noticeable for $K_{1.74}Pt(CN)_4 \cdot 1.8H_2O$ (12). The a.c. conductivity has been determined for $K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$ at 10^{10} Hz and at room temperature was the same as the d.c. value. Below 200K the a.c. conductivity decreased more slowly with decreasing temperature than the d.c. conductivity (10).

There is obviously a large anomaly between the optical reflectivity and Pauli paramagnetism studies that suggest metallic behaviour along the c-axis, and the conductivity results which indicate a semiconductor below 200K. Two theories have been proposed to explain this anomaly. In the interrupted strand theory the crystal is pictured as consisting of linear one-dimensional metallic strands of the platinum complex interrupted by insulating lattice defects. The conductivity is then controlled below 200K by a thermally activated process. The

activation energy is the energy required to transfer an electron from one metallic strand to a neighbouring strand. Alternatively, in the 'random potential' theory, complete delocalisation of the electrons along the whole length of the crystal is not expected because of the presence of anions (e.g. Br^-) or cations (e.g. K^+) in only a percentage of all the possible crystallographic sites along the platinum complex chain. This random presence of ions will, it is thought, produce a random potential which will have the effect of restricting the metallic electrons to finite lengths of the platinum atom chain instead of allowing them to move freely from one end of the crystal to the other. The behaviour of the crystal is then expected to be that of a one-dimensional amorphous semiconductor.

Both theories, therefore, picture a single crystal of these complexes as containing short chains of metal atoms, in which the electrons are delocalised, separated from one another by an area in which the electrons are localised. The reflectivity and paramagnetism are determined by the areas of the crystal in which the electrons are delocalised, whereas the electrical conduction below 200K is controlled by the process of the electron moving from one delocalised chain to the next delocalised chain. It is thought that the 'delocalised' metal chains consist of between 100 and 500 platinum atoms.

The conduction process at higher temperatures including the semiconductor-to-metal transition is not easily explained. It is clear that the thermally activated conduction process which controlled the conductivity below 200K is no longer the controlling process at room temperature. Whether at this higher temperature all the electrons have sufficient thermal energy to cross the inter-strand space or whether a new conduction mechanism begins to operate at this temperature is not known at present. Unfortunately, those complexes studied so far are hydrated and lose water just above room temperature, thus preventing conduction

studies above the insulator-to-metal transition.

Several of these partially oxidised metal chain compounds have been shown to undergo a unique oxidation reduction reaction under the influence of a d.c. field of above 150V/cm (13). Under these conditions a crystal of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30}\cdot 2.3\text{H}_2\text{O}$ changes colour at the anode from the original copper colour to give a white product $\text{K}_2\text{Pt}(\text{CN})_4\cdot x\text{H}_2\text{O}$. There is a sharp boundary between the two colours and bromine is expelled at the interface. The effect of the reaction is therefore to reduce the partially oxidised platinum complex to a platinum(II) complex. The occurrence of this reaction clearly sets a limit on the d.c. potentials that can be applied to these conducting complexes.

From the viewpoint of producing a one-dimensional metallic conductor the results so far are encouraging. It is clear that the platinum complexes described in this article exhibit this property over short distances within the crystal even though the whole crystal behaves as a semiconductor over a large temperature range. The "insulator-to-metal" transition which appears to occur at higher temperatures needs much further investigation and work on synthesising complexes in which this occurs at lower temperatures and on complexes possessing a greater thermal stability is being carried out. These complexes also possess an anomalously high dielectric constant which may find a practical application in the future. It has been suggested that these complexes may be capable of development as high temperature super-conductors and clearly their development as one-dimensional metallic conductors is a necessary step to this aim.

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Platinum Deposition on Sapphire and Alumina

SPUTTERED SUBSTRATES FOR FERROELECTRIC FILMS IN COMPUTER MEMORIES

An important factor in the successful development of sputtered thin ferroelectric films for computer memories is the availability of a substrate that is smooth, electrically conductive, refractory, and inert. Platinum films sputtered on to polished sapphire or smooth alumina chips meet this requirement but there is a problem of adhesion between the noble metal film and the oxide ceramic. Even chromium and titanium, which are often used as interface layers to promote adhesion, oxidise under the platinum during the prolonged heat treatment that converts dielectric to ferroelectric films at 950°C in a corrosive atmosphere.

S. F. Vogel and I. C. Barlow of I.B.M. Corporation's Systems Development Division at San Jose, California have developed a solution to the problem by sputtering platinum on to carefully cleaned and etched sapphire and alumina substrates to give strongly adherent films, and they have now described tests carried out to verify their results (*J. Vacuum Sci. Technol.*, 1973, **10**, (5), 843-846). Conventional sputtering of platinum had led to the film blistering and flaking during the heat treatment of the ferroelectric deposit at 950°C, and intermediate films of zirconium or titanium, which normally promote adhesion of noble metals to oxide ceramics or glasses, also failed during heat treatment.

The I.B.M. technique was developed empirically and consists of a two-stage deposition process followed by heat treatment. First oxygen is used as the sputtering gas for 22 minutes, giving a platinum deposition rate of 35 Å per minute. Then argon is used as the sputtering gas for a further 22 minutes, dur-

ing which the deposition rate increases to 180 Å per minute. It is essential to maintain the sapphire or alumina substrates during sputtering at a temperature of at least 580°C. The heat treatment in air is a controlled temperature rise over six hours to 930°C, maintenance at this temperature for two hours, and slow cooling for 12 hours.

Adhesion tests consisted of scratching specimens with a hand-held tool until failure occurred. Satisfactory adhesion was indicated by the smeared appearance of the platinum in the centre and on the edges of the scratch. Heat treated platinum films adhered much better than as-sputtered films. Crystal structure and topography of single-crystal sapphire, polycrystalline alumina and platinum films were studied by back-reflection Laue photography, diffractometry and scanning electron microscopy. On sapphire the platinum exists either as smooth single crystal material or as material with a dull fibrous texture oriented along the [111] direction. Platinum films on alumina were also fibrous.

While the main purpose of the platinum films was to serve as substrate to ferroelectric films, platinum has also been shown to be the most satisfactory material for contact electrodes deposited on to the exposed surface of the ferroelectric films. It was sputtered in argon to 3000 to 5000 Å on the initial dielectric films, followed by joint firing at 950°C, the temperature of conversion of the dielectric to the ferroelectric films. Alternatively, platinum dots can be deposited on converted films but heating at 600°C in air is then needed to produce satisfactory contact properties.

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