

Directional Electrical Conductivity in Platinum Complexes

MODELS FOR ROOM TEMPERATURE SUPERCONDUCTIVITY

The existence of a new class of compounds with a relatively high electrical conductivity along one axis has recently been reported (1) by Professor Perlstein of Johns Hopkins University. Potassium tetracyanoplatinate with a bromine addition is one of this class and other possibilities are listed in the table.

values for this type of compound as to stimulate further investigation.

The best results were obtained with bromine additions, which led to the compound $K_2Pt(CN)_4Br_{0.3} \cdot 2.3 H_2O$. This grows in the form of long needles, and crystallographic

Some Square Planar Platinum Metal Complexes of Mixed Valency and Possibly High Electrical Conductivity in One Direction	
Complex	Metal-Metal Distance Å
$H_{1.40}[Pt(C_2O_4)_2] \cdot 2H_2O$	2.80
$Li_{1.64}[Pt(C_2O_4)_2] \cdot 6H_2O$	2.81
$K_{1.64}[Pt(C_2O_4)_2] \cdot xH_2O$	2.82
$Mg_{0.82}[Pt(C_2O_4)_2] \cdot 5.3H_2O$	2.85
$Ir(CO)_{2.9}Cl_{1.1}$	2.85
$K_2Pt(CN)_4Cl_{0.32} \cdot 2.6H_2O$	2.88
$K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$	2.89

In crystalline form these compounds are characterised by the square planar arrangement of four ligands around the central metal atoms as shown in Fig. 1 (a). Here the squares are stacked on top of one another so direct interaction occurs between the metal ions perpendicular to the plane of the complex as shown in Fig. 1 (b). Square planar complexes have been known for many years but most of them are insulators with large band gaps.

Professor Perlstein's work has shown, however, that the platinum compound $K_2Pt(CN)_4 \cdot xH_2O$ has a resistivity in the metallic axis direction of about $2 \times 10^6 \Omega \text{ cm}$, which, although high by metallurgical standards, was so much lower than other reported

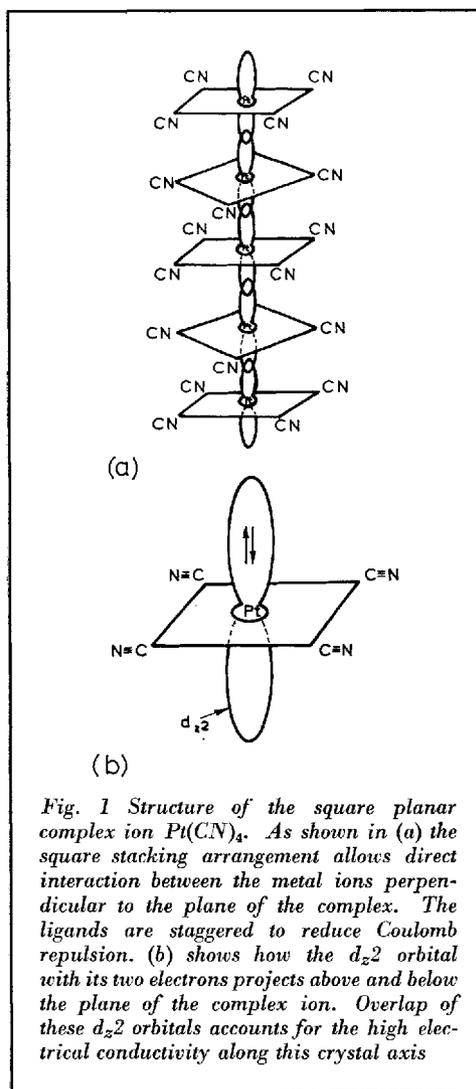
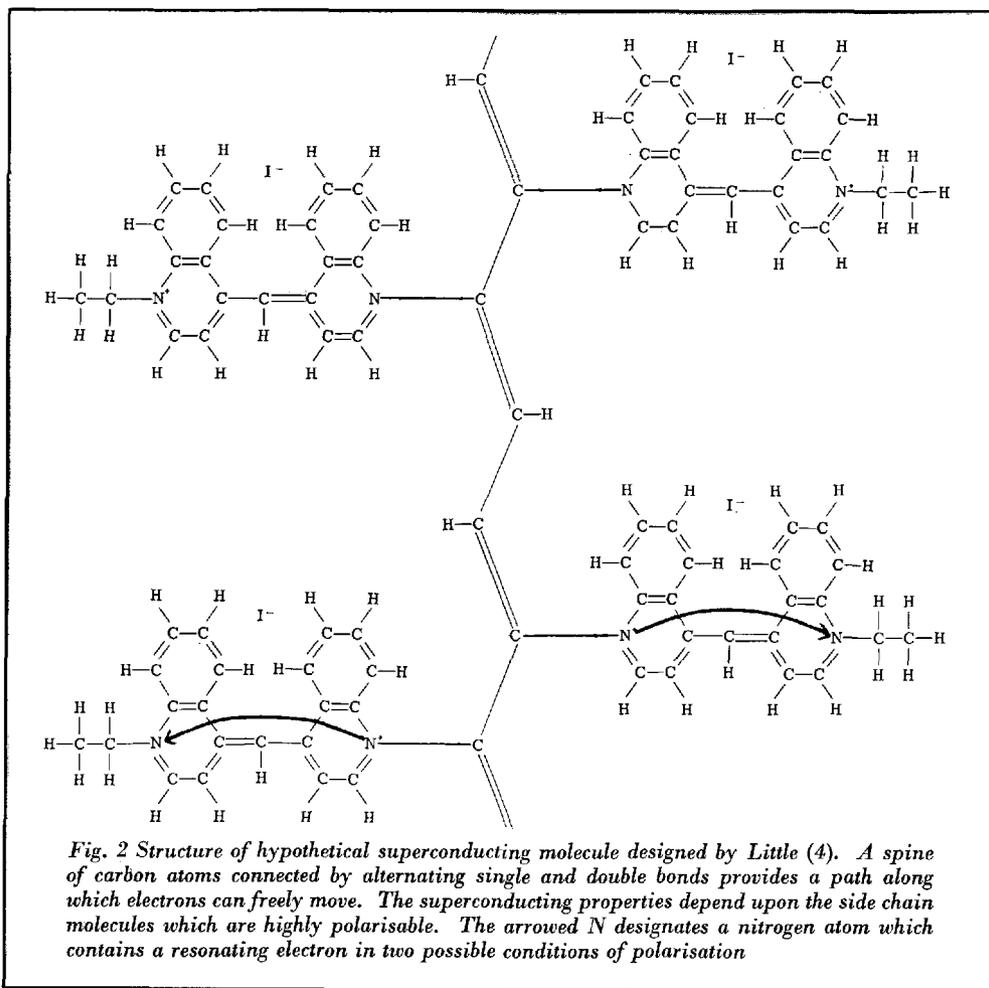


Fig. 1 Structure of the square planar complex ion $Pt(CN)_4$. As shown in (a) the square stacking arrangement allows direct interaction between the metal ions perpendicular to the plane of the complex. The ligands are staggered to reduce Coulomb repulsion. (b) shows how the d_{z^2} orbital with its two electrons projects above and below the plane of the complex ion. Overlap of these d_{z^2} orbitals accounts for the high electrical conductivity along this crystal axis



studies have shown that the $\text{Pt}(\text{CN})_4$ groups are stacked one on top of the other with a Pt-Pt separation of only 2.89 Å.

Crystals of the compound have a coppery appearance. Their average resistivity is about $0.25\Omega \text{ cm}$ at room temperature, and previously reported resistivity values of about $10^3\Omega \text{ cm}$ (2) were probably in error because of faulty measuring techniques.

The strong similarities which exist between the structure of these platinum complexes and those of the organic superconducting materials discussed by W. A. Little (Stanford University) (3, 4, 5) have encouraged speculation by both Perlstein and the press (6).

One of the molecular arrangements favoured by Little (4) is shown diagram-

matically in Fig. 2, and is characterised by a long central spine of carbon atoms on each side of which molecular side chains extend outwards, rather like the ribs of a human rib cage. The carbon spine is conjugated, having alternating single and double bonds along the chain and should, therefore, behave very like a metal with conduction electrons moving freely under the action of a potential gradient.

Electrons running along the spine of such a molecule would have the effect of polarising these side chains by inducing a positive charge at the end nearest the spine. This positive charge lags some distance behind the high speed electron which causes it, thus allowing the attraction of a second electron which is thereby coupled to the first. This

mechanism is analogous to that which is commonly used to explain the operation of normal transition metal superconductors (7).

Since polarisation involves merely the movement of a single electron in the side chain, rather than the vibration of comparatively massive metal atoms, high transition temperatures are to be expected from these organic long chain compounds. Little suggests that room temperature superconduction should theoretically be possible with the right type of molecule and concludes that dyes similar to diethyl-cyanine iodide, which is readily ionisable, should form a suitable base for the side arms component.

Although structural analogies can be drawn between these organic molecules and the square planar platinum complexes being studied at Johns Hopkins, the prospects for room temperature superconductivity are still very remote. The progress so far made, however, should not be underestimated and in this connection it may be of interest to mention the anisotropic electrical properties of the mixed oxidation state compound $[\text{Pd}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2, \text{Pd}^{\text{IV}}(\text{NH}_3)_2\text{Cl}_4]$ now being studied by workers at the University College of North Wales (8). This compound

has a chain structure with chlorine atoms bridging alternate Pd^{II} and Pd^{IV} atoms. The resistivity along the metallic axis is, however, approximately nine orders of magnitude higher than that found in Perlstein's compounds, due no doubt to the bridging halogen atom.

At the present time the importance of Professor Perlstein's work resides in the improved understanding it provides into the nature of the chemical interactions involved in square planar platinum complexes. The intimate relationships between his own molecules and those of Little might well be fruitful, however, and future developments will be awaited with interest. A. S. D.

References

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Miniature Palladium Diffusion Tubes for Chromatography

The use of palladium to purify hydrogen is well known throughout industry and Johnson Matthey have developed units capable of handling up to many thousands of litres per hour.

At the other end of the scale the California Institute of Technology's Jet Propulsion Laboratory at Pasadena has devised a miniature gas chromatograph with hydrogen as a carrier gas. A minute palladium tube allows the hydrogen to be removed as the gas stream emerges from the chromatograph column, the components of interest remaining with a second carrier gas for transmission to a mass spectrometer. Here a silver-palladium alloy tube removes the remaining hydrogen and samples arrive at the mass spectrometer

without loss. The aim of the Laboratory is to design a miniature gas chromatograph/mass spectrometer for use in future space probes landing on Mars to analyse the atmosphere of the planet.

Triangle Environmental Corporation of Raleigh, North Carolina, has adapted this work in its Protran concentrator for use with an ordinary gas chromatograph employing a mixed hydrogen carrier gas. The concentrator follows the chromatograph column and hydrogen passes out of the system through a selectively permeable palladium membrane. The sample becomes concentrated in the remaining gas which passes to the detector. It is claimed that chromatograph sensitivity is increased by up to 30 times or more.