Mixed-Valence Square Planar Complexes: A New Class of Solids with High Electrical Conductivity in One Dimension

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Square planar complexes of platinum are shown to have high, possibly metallic conductivity along one axis due to overlap between d_{z^2} orbitals of platinum in two valence states. The room-temperature Seebeck effect is small and positive which is interpreted as caused by a degenerate gas of holes.

We wish to report the existence of a new class of materials which have high, possibly metallic conductivity along one axis. $K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$ is one member of this class; other possible members are listed in Table I.

The common feature in this class is the square arrangement of four ligands (not necessarily all identical) around a central metal ion such that in the solid state the squares are stacked one on top of the other producing direct interaction between the metal ions perpendicular to the plane of the complex as shown in Fig. 1(b). Square planar complexes have been well known in chemistry for many years. Most of them are insulators with large band gaps[5] and intense charge-transfer absorption in the ultraviolet.

If we look at $K_2Pt(CN)_4$ in terms of the simple crystal-field model of four cyanide ions surrounding a Pt^{2+} ion in D_{4h} symmetry, we see that the d orbitals of the platinum ion, which can hold eight electrons, are split by the intense crystal field of the surrounding cyanide ions as shown in Fig. 2. The ordering of the lowest levels is, however, uncertain. We have placed them in the order given by Piepho, Schatz, and McCaffery.[6] In the more exact treatment of molecular orbital theory, one would take into account the σ- and π^*-type molecular orbitals formed by the cyanides with platinum. In either case one ends up with two electrons in the $a_{1g}(d_{z^2})$ orbital in the crystal-field theory or two electrons in an antibonding a_{1g}^* orbital whose wave function consists mostly of the platinum d_{z^2} orbital.

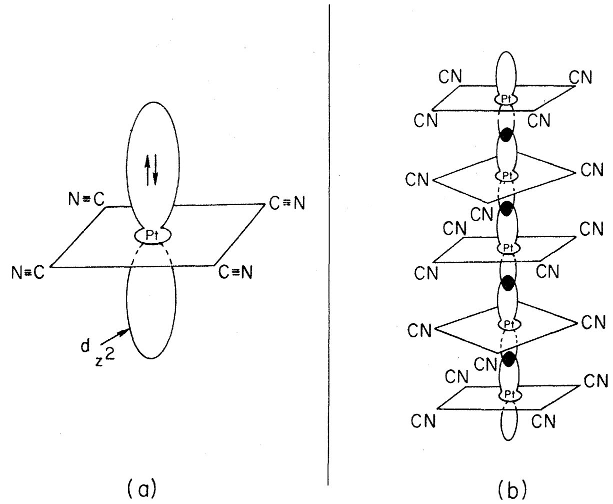
Table I. Some mixed-valence square planar complexes with possible metallic conductivity.

Material	Metal-metal distance (Å)	Ref.
$H_{1.60}[Pt(C_2O_4)_2] \cdot 2H_2O$ [a]	2.80	1,2
$Li_{1.64}[Pt(C_2O_4)_2] \cdot 6H_2O$	2.81	1,2
$K_{1.64}[Pt(C_2O_4)_2] \cdot xH_2O$	2.82	1,2
$Mg_{0.82}[Pt(C_2O_4)_2] \cdot 5.3H_2O$	2.85	1,2
$Ir(CO)_{2.9}Cl_{1.1}$ [b]	2.85	3
$K_2Pt(CN)_4Cl_{0.32} \cdot 2.6H_2O$	2.88	4
$K_2Pt(CN)_4Br_{0.30} \cdot 2.3H_2O$	2.89	4

[a] C_2O_4 is oxalate.
[b] $Ir(CO)_{2.9}Cl_{1.1} \equiv 0.95[Ir(CO)_3Cl] + 0.05[Ir(CO)Cl_3]$.

The d_{z^2} orbital with its two electrons points above and below the plane of the complex ion as shown in Fig. 1(a). Overlap of these d_{z^2} orbitals can thus produce a band which is completely filled and separated from the next empty band (formed by p_z overlap) by a large gap. Such a model was suggested by Miller[7] to account for the optical properties of other square planar complexes of platinum. For $Na_2Pt(CN)_4 \cdot 3H_2O$ the Pt-Pt distance is 3.63 Å.[8] From optical data it is predicted to be 3.35 Å in $K_2Pt(CN)_4 \cdot 3H_2O$.[9] We have measured the electrical conductivity of single crystals of $K_2Pt(CN)_4 \cdot xH_2O$ using a four-probe technique (two current leads and two potential leads painted directly onto the sample) and have found an average $\sigma = 5 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$.

What was of interest to us to support a band



(a) (b)

FIG. 1. (a) The d_{z^2} orbital of $Pt(CN)_4^{2-}$ with two electrons. (b) Overlap of d_{z^2} orbitals between stacked complex ions. The ions are staggered to reduce the Coulomb repulsion between ligands.

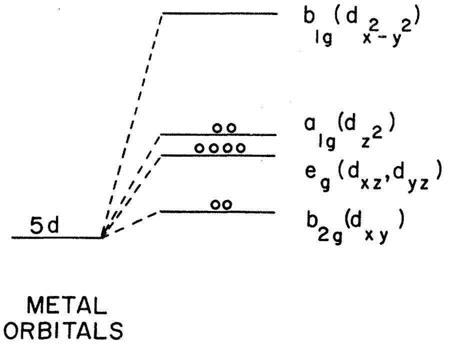


FIG. 2. Ordering of d-orbital energy levels in a crystal field with D_{4h} symmetry. Levels up to a_{1g} (d_{z^2}) are filled.

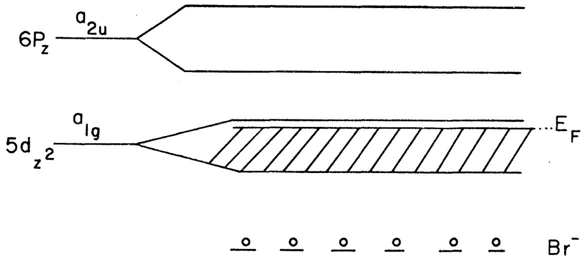


FIG. 3. Band formation due to overlap of a_{1g} (d_{z^2}) orbitals between complex ions. Br^- energy lies below the d_{z^2} band which is $\frac{5}{6}$ full. The next empty band is formed by overlap of the a_{2u}(p_z) orbitals on each complex ion.

picture along one dimension was to add donors or acceptors to the crystals in order to reduce the activation energy for conduction and thereby increase the electrical conductivity. The addition of "donors" to a complex of Pt(II) is chemically equivalent to reducing Pt(II) to Pt(I) or Pt(0). While such low-oxidation-state complexes are known, they are highly air unstable; and, thus, we have not pursued their preparation at this time. The addition of "acceptors" is equivalent to oxidizing Pt(II) to Pt(IV) which is a well-known air-stable oxidation state for platinum. This oxidation state is easily prepared by the addition of Br_2, Cl_2, H_2O_2, or any other oxidant to aqueous solutions of $K_2Pt(CN)_4$. With the use of Br_2 this produces $K_2Pt(CN)_4Br_2$. Upon mixing the oxidized solution with the unoxidized solution in the ratio 1:5, crystals with the composition $K_2Pt(CN)_4Br_{0.3} \cdot 2.3H_2O$ can be obtained by evaporation.[10] The strong acceptor nature of bromine will put their energy levels below the d_{z^2} band. If the ordering of the crystal-field-split states shown in Fig. 2 is correct, addition of bromine will produce the situation in which the d_{z^2} band is partially empty as shown in Fig. 3. The same situation could be produced for a different ordering provided the highest filled state in $K_2Pt(CN)_4 \cdot xH_2O$ is the top of the d_{z^2} band. Since there is one bromine atom for every three platinum atoms, each of which contributes two electrons to the d_{z^2} band, the band will be $\frac{5}{6}$ full. Based upon the expected narrowness of d bands, the band curvature should occur gradually so that the $\frac{5}{6}$-full band is predicted to be a hole metal.

$K_2Pt(CN)_4Br_{0.3} \cdot 2.3H_2O$ grows in the form of long needles. The x-ray crystal structure[4] shows that the $Pt(CN)_4$ groups are stacked staggered one on top of the other along the needle axis with a Pt-Pt separation of 2.89 Å which is considerably less than in $K_2Pt(CN)_4 \cdot 3H_2O$ (3.35 Å). Figure 4 shows the unit cell projected along (001) and (010) with the bromine, water, and potassium ion positions indicated. The stoichiometry of the material appears to be such that only $\frac{3}{5}$ of the total bomine sites are occupied. It is not known whether the bromines are ordered or occupy the available sites randomly; but, presumably, this should have some effect on the periodic potential which produces the d-band structure.

The crystals have the visual appearance of metallic copper. The optical absorption spectrum is highly polarized along the z axis (needle axis) with an absorption peak occurring at about 5700 Å (17 500 cm^{-1}).[11] Perpendicular to the needle axis the crystals appear visually to be transparent. The average room-temperature electrical conductivity is 4 Ω^{-1} cm^{-1} for six samples.

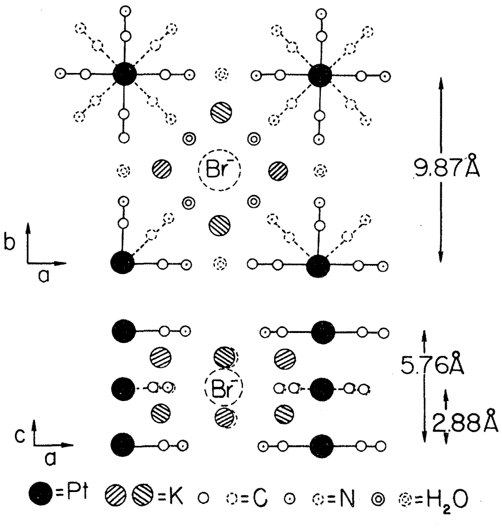


FIG. 4. $K_2Pt(CN)_4Br_{0.3} \cdot 2.3H_2O$ unit cell projected along the c and b axes. The complex ion stacking is evident (after Krogmann and Hausen).

We believe that this is presently the highest electrical conductivity exhibited by complexed metal atoms. A previous report of $10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for the electrical conductivity was based on a two-probe measurement using silver paste and mercury electrodes.[4] We have found Aquadag to be the most reliable contact for this material.

We have also measured the Seebeck coefficient against copper and found a room-temperature value of $+12\ \mu\mathrm{V}/°\mathrm{K}$ (where the sign is for the cold junction). In the simplest interpretation, the low positive value would indicate a degenerate gas of holes.

It is interesting to note that these long-chain complexes are structurally similar in many respects to a model organic compound for a high-temperature one-dimensional superconductor proposed by Little.[12] Based on the closer metal-metal distances of the other complexes listed in Table I and the uncertain purity of the cyanide complexes, there is reason to believe that long chain complexes such as these should have even higher electrical conductivity than found here.

We are presently continuing our studies on the temperature dependence of the electrical conductivity, Seebeck effect, and Hall effect of $K_2Pt(CN)_4Br_{0.3}\cdot 2.3H_2O$ as well as of $Ir(CO)_{2.9}Cl_{1.1}$ and $Mg_{0.82}[Pt(C_2O_4)_2]\cdot 5.3H_2O$ and will report on the results in the near future.

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Evidence for a First-Order Structural Transformation in Nb_3Sn

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We present experimental evidence that the structural transformation observed in Nb_3Sn is first order, as predicted by theories which invoke a band Jahn-Teller mechanism for the lattice instability. The magnitude of the spontaneous lattice distortion at the transition temperature is in excellent agreement with the theory.

The nature of the structural transformation in the β-W compounds V_3Si and Nb_3Sn has been the subject of considerable theoretical and experimental interest. Calculations based on independent electron sub-band models have unambiguously predicted that the cubic-to-tetragonal transition is first order, weakly so for V_3Si[1] but quite strongly for the case of Nb_3Sn.[2] However, the absence of an observable latent heat[3] and hysteresis[4] at the transition has been interpreted as evidence that the transformation is actually second order. Since a transition in which the tetragonal strain $\epsilon = \frac{2}{3}(1-c/a)$ is the only order parameter is necessarily first order,[5] the possibility of the existence of a second order parameter which is coupled to ϵ has been explored. Soft optic modes of particular symmetries have been proposed,[6] and calculations[7] based on a successful band model have predicted instabilities in these modes. Thus far, no direct experimental evidence for such an instability exists. Recently, Pytte[8] has reformulated the theory for acoustic modes, us-