ORGANIC SUPERCONDUCTORS:
SYNTHESIS OF THE ORGANIC COMPOUND PPNSeCN
(Bis-triphenylphosphine-iminium Selenocyanide)

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## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF ILLUSTRATIONS.</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACTS</td>
<td>v</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>LITERATURE REVIEW</td>
<td>3</td>
</tr>
<tr>
<td>MATERIALS AND METHODS.</td>
<td>9</td>
</tr>
<tr>
<td>Bis(triphenylphosphine)iminium cyanide</td>
<td>9</td>
</tr>
<tr>
<td>Bis(triphenylphosphine)iminium selenocyanide</td>
<td>9</td>
</tr>
<tr>
<td>Electrolytic cell growth</td>
<td>10</td>
</tr>
<tr>
<td>RESULTS</td>
<td>12</td>
</tr>
<tr>
<td>DISCUSSION</td>
<td>13</td>
</tr>
<tr>
<td>LITERATURE CITED</td>
<td>16</td>
</tr>
</tbody>
</table>
### TABLE OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The Meissner Effect</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>TMTSF Molecule</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>PPN$^+$SeCN$^-$ Molecule</td>
<td>15</td>
</tr>
</tbody>
</table>
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ABSTRACT

The bis(triphenylphosphine)iminium salt (PPNSeCN) was synthesized from PPNCl, KCN and Se. This salt was then grown electrochemically with the organic molecule TMTSF. The anion chosen was also selected for its unit cell volume and its polarity.
INTRODUCTION

Superconductivity is a state in which materials offer no resistance to the flow of electricity. A Dutch physicist, Heike Kamerlingh Onnes first discovered superconductivity in 1911 in frozen mercury while attempting to liquify Helium gas (1,2). This sudden change to zero resistance occurred below the metals so called critical temperature, the temperature where the transition to superconductivity takes place which for mercury is $4.15^0 K$. Since then many different metals and several hundred alloys composed of these metals have been identified as superconductors (1). The technological potential of perpetual motion machines based on the principle of superconductivity is limitless, however, the outlook for high temperature metallic superconductors is dismal. Extensive research suggests it is unlikely that an alloy will ever be found with a transition temperature much higher than $20^0 K$ (1).

The organic compound, TMTSF (tetramethyl tetraselenfulvalene), has been electrochemically combined with certain anions, producing superconductors of the formula, $(TMTSF)_2X$. In 1979, Bechgaard, Jerome and Ribault found $(TMTSF)_2PF_6$ superconducting at $1.9^0 K (-272^0 C)$ and 12 kbar of pressure (6). Since then other superconducting salts have been found where $X = (\text{ToF}_6^-, \text{AsF}_6^-, \text{SbF}_6^-, \text{ReO}_4^- \text{and ClO}_4^-)$. Of these $(TMTSF)_2\text{ClO}_4$ is the only natural atmospheric pressure organic superconductor.

By the use of a method that can predict the unit cell volume of the TMTSF salt of a particular anion, the design and synthesis of TMTSF deriv-
itives with unit cell volumes comparable to \((\text{TMTSF})_2\text{ClO}_4\) are currently under investigation. In 1981, the X-ray and Neutron Diffraction Research group at Argonne National Laboratories began a structure analysis of TMTSF crystals supplied by Klaas Bechgaard. Soon after, an investigation on the synthesis and characterization of organic superconductors commenced.

The present work, as part of Argonne's Student Research Program, consisted of the synthesis of bis(triphenylphosphine)iminium selenocyanide \((\text{PPN}^+\text{SeCN})\) and the crystal formation with TMTSF.
Establishing superconductivity in an organic solid is a remarkable phenomenon because the great majority of organic materials are electrical insulators. Long before their discovery, the technological potential of superconductors has been obvious. If they could perform the phenomenon at less severe temperatures than what has been found, lossless power transmission, more efficient electric motors and powerful electromagnets could become available. Superconducting circuit elements could be used in supercomputers. The speed of a computer is fundamentally limited by its size which is restricted by the ability of its circuit elements to dissipate heat. In the superconducting state, a stream of electrons can flow without encountering any resistance in the form of friction. The current can then persist indefinitely without any further energy input. A superconducting element could in fact, respond to a signal much faster than any semiconducting device now used.

Superconductors exhibit a magnetic effect, called the Meissner effect, first observed by two German physicists in 1933 (4). The observation was that a superconductor in a magnetic field would generate its own internal field and expel the external field once it is cooled below the transition temperature to the superconducting state. The lines of force of the external magnetic field, bend around the surface of the superconductor instead of passing through it. This effect implies a technological application: a roadway made of superconducting material would repel a
magnetic field generated by a vehicle. The vehicle would float above the roadway on a magnetic cushion and would move nearly without friction.

Figure 1. The Meissner effect.

The breakthrough on the theory of superconductivity came in 1957 when John Bardeen, Leon Cooper and John Schraffer, in the U.S., developed a model based on quantum mechanics (1,2). In the BCS model, superconductivity arises when electrons in a conductor form loosely bound pairs, from electron-photon interaction called Cooper pairs. The electrons form a loose pair, each made up of electrons with equal and opposite momentum and spin held together by an attractive interaction. These electrons are the outer electrons in the orbits called valence electrons and they are the least tightly bound electrons in an atom. This apparent contradictory "attractive" interaction between like charged ions when one electron produces a ripple in the lattice (from the electrostatic attraction between the electron and the positively charged ion) causing a region of net positive charge where a second electron will be attracted forming a Cooper pair. Because they are bound in pairs, the electrons are less
easily scattered by the lattice and the electric current will encounter less resistance to its flow. These pairs are not formed above the critical temperature because here the photon energy is not great enough to cause an electronic interaction sufficient to overcome the repulsive coulomb interaction of the electrons. As a result the electrons are not attracted to each other and there is no Cooper pair formation.

Since the formation of the Cooper pairs depends upon irregularities of the atomic lattice, the critical temperature for superconductivity is related to the stiffness of the lattice and its resistance to deformations are large compared with ones caused by thermal vibrations and the critical temperature is high. There is an argument that the softening of the lattice may establish an upper limit to the critical temperature for superconductivity (4). As the lattice becomes softer, its vibration frequency decreases which tends to inhibit the formation of Cooper pairs, an effect that may become dominant between 25 and 30° K. As new superconductors have been discovered, the average value of the critical temperature has increased by 0.3 degrees per year, the highest being an alloy of niobium and germanium (Nb₃Ge) at 23.2° K (2). This lattice softening effect may account for the failure to find any substance with a critical temperature higher than this.

Electrical conduction in a superconductor is caused by the net motion of the center of mass of the Cooper pairs. If no current is flowing through the material, the momentum of each pair is zero and the velocities of the center of mass of each pair must be exactly zero. When there is a current in the material the electrons in each pair move in such a way that the centers of mass of all the Cooper pairs have the same constant momentum. Every motion of one electron that threatens to break up the
Cooper pair must be compensated for by its partner so that equilibrium is always maintained.

In an ordinary metal, electrical conduction is caused by the net motion of individual valence electrons. The resistivity in this metal is due to scattering of moving electrons by imperfections in the atomic lattice and by thermal vibrations of the lattice at any temperature above absolute zero. The scattering impedes the current and reduces the energy of the system which causes a change in the stored vibrational energy of the lattice. The resistivity of a perfectly regular metal lattice would theoretically be zero because at this temperature there is no vibrational energy in the lattice available for scattering electrons.

On the other hand, in a superconductor, the electrical resistivity can be zero at a finite temperature because once the Cooper pairs are put into motion by an electric field, they acquire a net momentum. This momentum cannot decay through scattering because a redistribution of an electron requires more energy than the vibrational energy at low temperatures.

In 1964, W.A. Little in the U.S., with the idea of superconductivity at room temperature in mind, proposed an alternative mechanism for the formation of Cooper pairs which does not depend upon lattice distortions. He proposed using a spine of carbon atoms to act as a conducting path for Cooper pairs and organic molecules attached to the spine would be the deforming lattice, each organic molecule having loosely bound valence electrons. A high critical temperature could be attained because a region of enhanced positive charge on the molecules closest to the carbon spine is created by the passage of an electron which will be attracted to a second electron moving along the chain. This is caused by a dis-
placement of an electron in the hydrocarbon molecule instead of by the
displacement of an atom in the lattice.

To date only a few organic molecules have been found that are used
to build superconducting solids. Among their features is a large planar
skeleton consisting mainly of carbon, nitrogen, sulphur and selenium.
The valence (pi electrons) are found above and below the planar framework.
The molecules can stack together like pancakes and the electrons will
form energy bands which can cause electrical conductivity from one plane
to another when electrons are removed from or added to the energy bands.

One of the first molecules of this type to be synthesized was TCNQ
(7,7,8,8 tetracyano-p-quino dimethane) in 1960 (6). This molecule is
electron poor and is not able to conduct an electric current. All the
TCNQ molecules have the same affinity for electrons, so there is no ten-
dency for electrons to move from one TCNQ molecule to another. In 1973,
it was combined with "electron rich" TTF (tetraphiofulvalene) forming
TTF-TCNQ. In the solid form the electrons are donated from the TTF to
the TCNQ stack and the material is conductive. To modify the electron
donating properties of TTF, heavier selenium atoms were substituted for
the sulfur atoms in TTF to make TSF (tetraselenofulvalene ) and from this,
Klaas Bechgaard of the University of Copenhagen made tetramethyl-TSF or
TMTSF. A compound was made with DMTCNQ (2,5 dimethyl TCNQ) called TMTSF-
TCNQ. These crystals conduct current at room temperature in a way similar
to TTF-TCNQ, but the material becomes an insulator below 41^\circ K. It was
found that if pressure was applied to the crystals and the material cooled,
it became a conductor at 4^\circ K, with ten times the conductivity of TTF-
TCNQ. Because the conducting properties of this complex were dependant
mostly upon the TMTSF molecule a separate study of this compound was initiated.

To make crystals of high purity, neutral TMTSF molecules are dissolved in an organic solvent, either TCE (1,1,2 trichloroethane) or THF (tetrahydrofuran) and a salt is added that releases negatively charged ions. These are put in either side of an electrochemical H-cell, as are two platinum electrodes and an electric current is conducted through the apparatus. At the positive electrode, electrons are removed from the TMTSF molecules to form positively charged molecules. These combine with a neutral TMTSF molecule and with one of the negatively charged ions and separate as an insoluble salt. This is how (TMTSF)$_2$X salts are prepared where X represents a negatively charged ion such as (SeCN$^-$) in this work.

The (TMTSF)$_2$X salts have unusual properties. Unlike other stacks of organic molecules such as TTF-TCNQ, most of their salts remain highly conductive well below 20 K. The transfer of electrons from TMTSF molecules to other molecules in the solid and the arrangement of the negatively charged ions in the crystal prevent susceptibility to distortions introduced by the charge density wave. If an organic conductor is not susceptible to such distortions, the material becomes a superconductor instead of an insulator at low temperatures. Recently an organic superconductor based on a different organic radical has been discovered, namely bis (ethylenedithiolo)tetrathiofulvalene (BEDT-TTF).
MATERIALS and METHODS

1. Bis(triphenylphosphine)iminium cyanide

\[ \text{PPN}^+\text{Cl}^- \text{aq} + \text{KCN}_\text{aq} = \text{PNPCN} + \text{KCl} \]

Initially, 2.8 g of PNPCl (Aldrich)* were dissolved in 200 ml water and added to a solution of 10 g of KCN (Aldrich)* dissolved in 50 ml water. The solution was stirred for 15 min at room temperature. A thick white precipitate formed which was saved after vacuum filtration. The precipitate was put in the freezer for 18 hr. The yield was 5.4 g.

2. Bis(triphenylphosphine)iminium selenocyanide

\[ \text{PNP}^+\text{CN}^- + \text{Se}_{\text{solid}} \xrightarrow{\text{acetone}} \text{PNP}^+\text{SeCN}^- \]

This step was performed with acetone under a dry box purged with nitrogen. If oxygen was allowed to enter, a yellow to orange solution was obtained suggesting that ionic cyanate was formed.

The 5.4 g of PNPCN was dissolved in 270 ml acetone (Merck)** to which 6.75 g of selenium was added. It was heated to 50°C under nitrogen for one hr. The solution was elutriated, saving the filtrate. It was then precipitated in a glass beaker by adding acetone and then diethyl ether (Merck)** dropwise along the side with a disposable pipette. This

** Merck and Co. Inc., Rahway, New Jersey 07065.
was a process of recrystallization which increased purity of the crystals. The solution was refrigerated overnight to promote crystallization after which it was filtered, saving the precipitate. The crystals were then dissolved in acetone, heated then hot filtered saving the filtrate. There was a lot of selenium present as black particles in the white crystals so the solution was hot filtered again then precipitated again with acetone and diethyl ether (second recrystallization).

The crystals were taken from the freezer and filtered, saving the crystals. They were dissolved in acetone, hot filtered, recrystallized for the third time and placed in the freezer. A sample was sent out for analysis, however, the yield was not good so a fourth recrystallization was attempted.

Because of the impure yield, the acetone was run through a column with a molecular sieve and fiberglass then suctioned through a fine fritted funnel. This will remove some of the impurities. The crystals were dissolved in the purified acetone then transferred to a large test tube and recrystallized using diethyl ether and acetone. This process took place in the dry box, where the crystals remained under nitrogen for five days hoping to seed out more product in the sample. The solution was suctioned filtered then put in the vacuum dessicator for a week.

3. Electrolytic cell growth of Tetramethyl tetraselenafulvaline selenocyanide.

The crystal growing apparatus consists of a glass H-cell with a fine porous slit between each side and two platinum electrodes. This is connected to a power supply with a 0 to 5 microamp range. The H-cell is kept in a thick styrofoam box maintained at a constant temperature of
11

23°C.

Before each use the cell is cleaned and dried following these steps: the cell is placed in aqua regia for several days. Distilled water is suctioned through the frit by a water aspirator three times on each side, changing the water each time. Triple distilled water, then methanol are drawn through in the same manner. The cell is then dried in an oven at 125°C for one day.

The platinum electrodes are also cleaned before each use. They are placed in 1M sulfuric acid and connected to a current of 2.5 volts for 4 min. The positive terminal of the battery is connected to the anode and the negative terminal to the cathode. A switch is made for 4 min and the leads are switched back to the original connection for 8 min. The electrodes are placed in triple distilled water then methyl alcohol each for 10 min then allowed to air dry.

To set up a cell for crystal growth, 1.5 mmoles of PPNSeCN are dissolved in 10 ml of THF. The THF is distilled for several days then dried by filtering through a column of alumina (Al₂O₃). Next, 0.06 mmoles of TMTSF are dissolved in 5 ml of THF then poured into the anode side of the H-cell. Part of the bis(triphenylphosphine)iminium salt is added to the cathode and anode compartments of the H-cell until each side is the same height. The cathode and anode are then purged under argon using a disposable pipette before the platinum electrodes are capped securely on each side. The electrochemical cell is now ready for crystal growth after connecting the electrodes with a constant current regulator. The initial current being set at 1.0 microamps. The salt sample was dried for several days at 100°C, then placed in a vacuum dessicator for a week.
RESULTS

The sample was sent to Midwest Microlabs* for an analysis which was as follows:

- molecular weight: 643.573
- melting point: 195–197°C

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<thead>
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<th>% composition</th>
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<tbody>
<tr>
<td>phosphorous</td>
<td>8.17</td>
<td>9.62</td>
</tr>
<tr>
<td>carbon</td>
<td>69.08</td>
<td>69.05</td>
</tr>
<tr>
<td>hydrogen</td>
<td>4.68</td>
<td>4.70</td>
</tr>
<tr>
<td>nitrogen</td>
<td>4.37</td>
<td>4.35</td>
</tr>
<tr>
<td>selenium</td>
<td>**</td>
<td>12.27</td>
</tr>
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The (TMTSF)$_2$SeCN crystals were weighed after harvesting, yielding 87%. The electric current was discontinued after the TMTSF solution loses its pink color, signifying the end of the reaction. The crystals from the anode were washed from the electrodes into a suction funnel using THF and the remaining solution in the anode was poured into the filter. The funnel was covered with filter paper and vacuum filtered for 1 hr after which the crystals were placed in a glass vial and stored in the vacuum dessicator.

* Midwest Microlab Ltd., 7212N. Shadeland Ave., Indianapolis, Indiana 46250.

** Midwest Microlabs were unable to do an analysis for selenium.
X-ray crystallography studies on the \((\text{TMTSF})_2\text{SeCN}\) crystals were done at Argonne National Laboratories to determine whether the typical 2:1 theoretical ratio (2 TMTSF to 2 SeCN molecules) existed. Normally if this ratio exists, additional tests are done to determine superconductivity. In this case the results were negative, consequently, superconductivity tests were not performed.

If an error was present, it may have been the result of experimental procedures. All operations with \(\text{PNP}^+\text{CN}^-\) in acetone were to be void of oxygen and done under nitrogen. The dry box in our laboratory was less than 100% efficient in that there were several routes for oxygen to enter the system. Impurities may have been gained and molecules may have been lost as a result of four crystallizations and even more filtrations and transfers. Errors may also have occurred through cleaning procedures.

The process of achieving a pure analysis from a salt as well as a perfect ratio from a crystal is a long and tedious process. The synthesis of \(\text{PPN}^+\text{SeCN}\) and the crystal formation with TMTSF may be attempted again at Argonne Laboratories but at present whether or not the \((\text{TMTSF})_2\text{SeCN}\) molecule has the ability to superconduct is still unknown.
TMTSF MOLECULE (Fig. 2)
PPN$^+\text{SeCN}^-$ MOLECULE (Fig. 3)
REFERENCES CITED


