FIRST ANNUAL TECHNICAL REPORT

August 1, 1970 July 31, 1971

NEW SUPERCONDUCTORS

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CENTER FOR MATERIALS RESEARCH

STANFORD UNIVERSITY • STANFORD, CALIFORNIA

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I. INTRODUCTION

The objective of this program is to study the theoretical and synthetic problems of producing higher temperature superconducting materials. The program consists of four principal sections: a theory section concerned with the calculations of the effective electron-electron interaction in the vicinity of large organic molecules, calculation of Coulomb screening, the extension of band theory methods to linear systems and the development of means of using these properties for the calculation of the transition temperature of any superconducting phases; a synthesis section involved in the synthesis of transition metal linear organo-metallic systems of crystalline or covalently bound structures and with special ligand systems for control of the electronic environment of the metal atoms; an x-ray section for determining the structure of crystalline samples; and an experimental section for determining the material parameters of the prepared materials as functions of temperature and pressure.

The initial phase of the program has been directed to each of the theoretical problems mentioned above and to developing synthetic methods for preparing various classes of linear conducting materials. Attention has been directed to the problem of obtaining an understanding of the basic electronic solid state physical properties of single crystal linear organo-metallic conductive chains. Likewise, attention has been turned to the problem of obtaining information on the band edge from infra-red transmission studies on these Krogmann type materials.

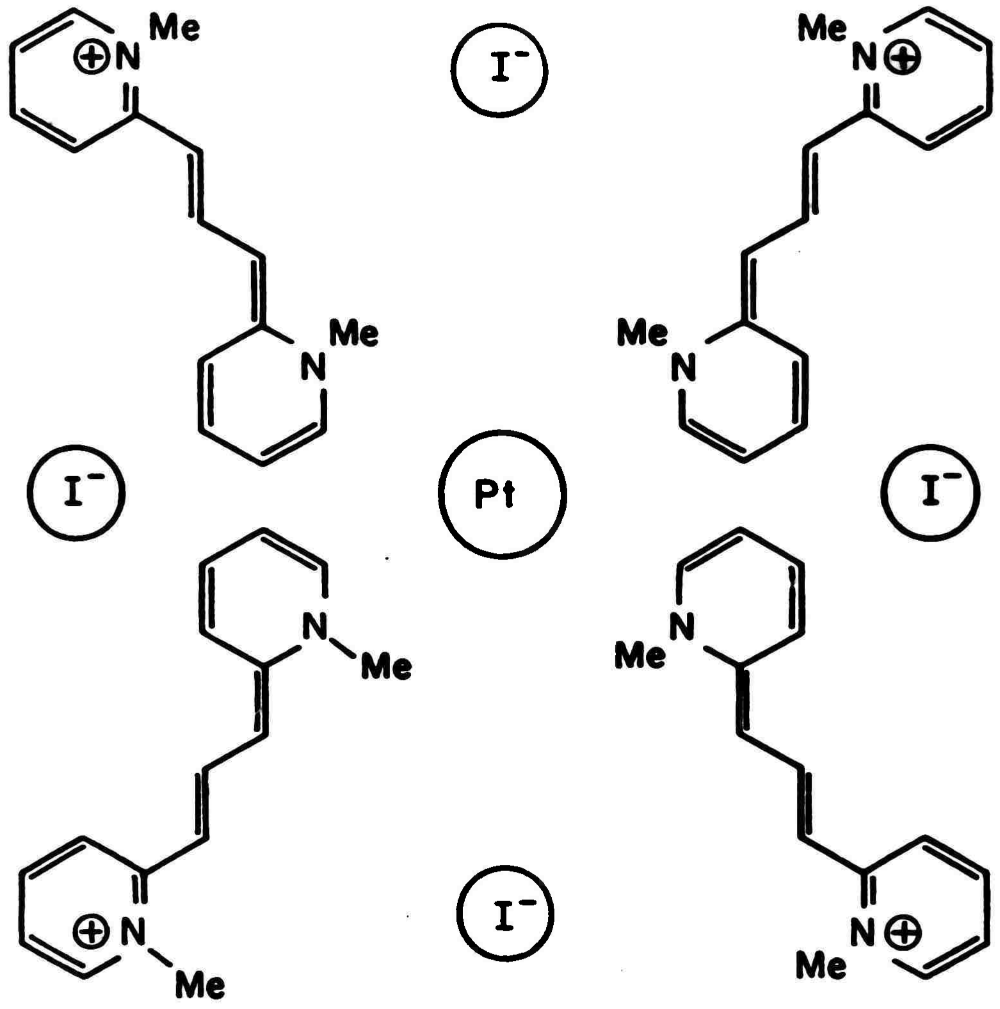


Fig. 1 Assumed dye configuration in unit cell. Glyoxime-chelate structure has been omitted.

II. THEORETICAL PROGRAM

Earlier we described a diagrammatic technique which allowed one to calculate to good accuracy the effective electron-electron interaction near a single polarizable dye molecule (Phys. Rev. B 4, 817, August 1971). These methods have now been extended to arrays of dye-molecules such as would be formed by chelating a linear chain of transition metals, such as found in the Krogmann salts, to a complex to which were attached dye molecules. The glyoxime system described in Appendix A represents the kind of complex which we have in mind. The single intense absorption band of a single dye develops into a band of levels when the dyes are brought close enough to one another to interact significantly. Our first problem has been to compute the energy levels and wavefunctions of these exciton bands. A formal computation of this is done by carrying out a configuration interaction (C.I.) calculation for each state of given exciton wave vector q.

We have considered the unit cell structure illustrated in Fig. 1 using the known bond length and angles for the glyoxime units and for the dye molecules. We have considered the situation with the Pt-Pt distances in the chain of 3.4Å and with only one Pt atom/unit cell. It is quite possible that the compound might in fact form a structure with two Pt atoms/unit cell with the second complex rotated through 90° about this axis, however, this is expected to make a negligible difference to the results obtained.

The energy levels of the dye and the many-body corrected transition densities were computed using the methods developed earlier. The result obtained is shown in Fig. 2. Noting that the principal absorption of the isolated dye lies at 1.89eV one sees that the dye-dye interaction results in a significant shift of the absorption in the array. For such an array the levels near q = 0 could be observed by optical absorption. The middle two levels are allowed

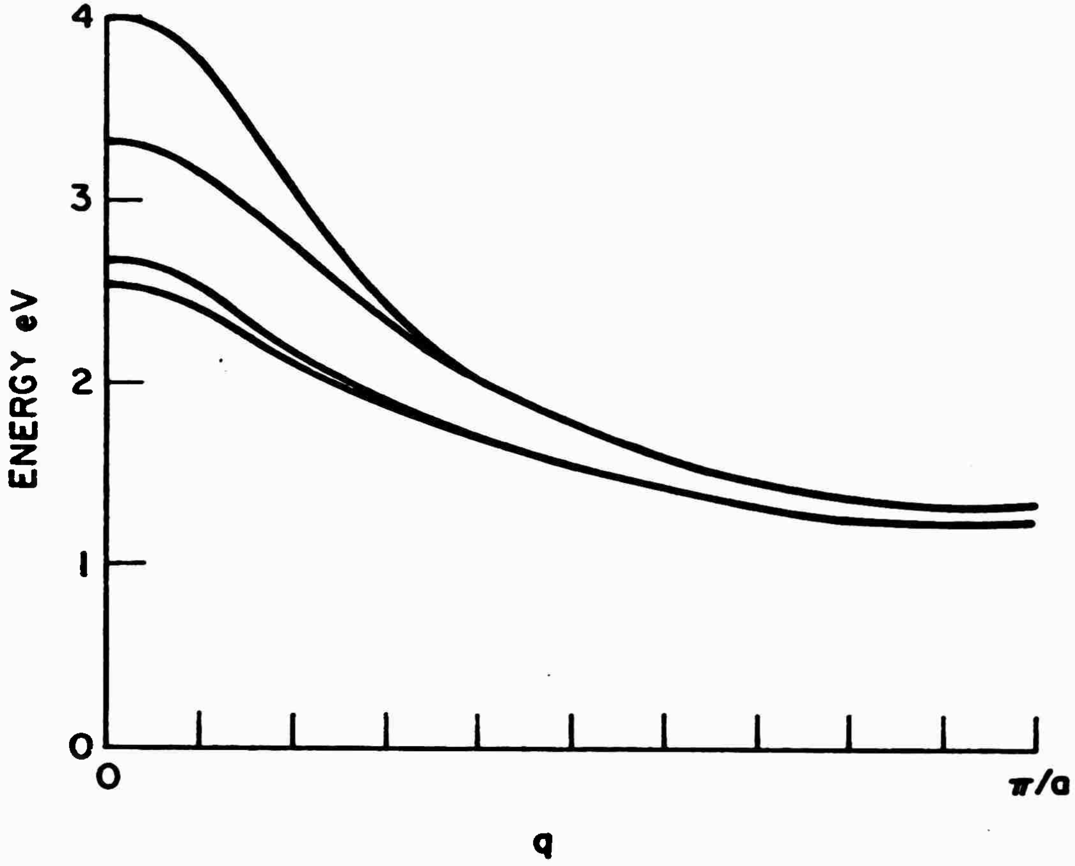


Fig. 2 Calculated exciton energies of dye arrays for wave-vectors, q along Pt chain direction.

while the upper and lower levels are forbidden to first order.

With this information available on the energies and wavefunctions of the exciton states it was now possible to calculate the effective electron-electron interaction in the vicinity of the array of molecules. For this we need to know the extent to which the higher excitations of the dye screen the Coulomb field. A reasonable approximation can be made in this case for these higher excitations have a transition density which has a rather small spatial extent in the molecule so that the dye-dye interaction is very weak. The resultant exciton band is narrow and one can thus ignore this small perturbation upon the energy levels of an isolated dye. By making this approximation the C. I. calculation for all the higher levels is avoided without significant loss of accuracy.

Our procedure has been to proceed as follows. We treat the electrons in the Pt-chain or spine in the LCAO approximation and calculate the Coulomb interaction for a momentum transfer q. In order to do this we need to know γ_{11} for Pt atoms i.e. the interaction between a pair of electrons on the same Pt atom. Using the Pariser approximation which relates γ_{11} to the ionization energy and the electron affinity we compute γ_{11} to be 6.03eV for Pt. We use this then in the Mataga-Nishimoto formula, $e^2/(r+a)$ for the bare interaction, where $\frac{e^2}{a} = \gamma_{11}$. For this we have used the bare Coulomb interaction but have considered only short chains of about 30Å in length in view of the computational cost. For q appreciably less than $1/30\ A^{-1}$ we expect the result to be virtually independent of the length of the chain. However, for large q we expect a significant error because as $q \rightarrow 0$ the interaction diverges for a single chain. To obtain correct results near $q=0$ for the physical situation in the Krogmann salts in which we have a parallel array of linear chains, it is essential that the screening of these adjacent chains be taken into account. This is our prime problem at the moment and we will discuss it again later.

Secondly, we calculated the screening of the Coulomb field which results from the response of the higher energy excitations of the dye. This is done in the approximation discussed earlier whereby we neglect the dye-dye interaction. For this calculation we again use the bare Coulomb interaction rather than the spine-screened interaction. These results are expected to be less affected by this approximation for the spine-dye-spine interaction is proportional to the square of a dipole interaction and thus falls off very rapidly with distance even in the absence of screening.

Then finally we calculate the frequency-dependent exciton interaction arising from the low-lying excited states of the dye taking into account the exciton energies and wavefunctions. The results obtained for each of the above terms is given in Fig. 3. There are several points worth stressing.

First, the net electron-electron interaction for small values of q is significantly reduced by the presence of the dyes. For the case considered here the interaction is only slightly positive, however, we have neglected the screening of the Coulomb field by the spine-electrons and though this would greatly weaken the main Coulomb term it would also weaken to some extent the excitonic term. It is thus of prime importance to determine with reasonable accuracy the screening of the adjacent chains.

Secondly, we see that the excitonic interaction falls off quite rapidly with increasing q so that at momentum transfers comparable to the reciprocal of the Pt-Pt spacing it is negligible. This is reasonable in view of the large separation between dye and Pt atom.

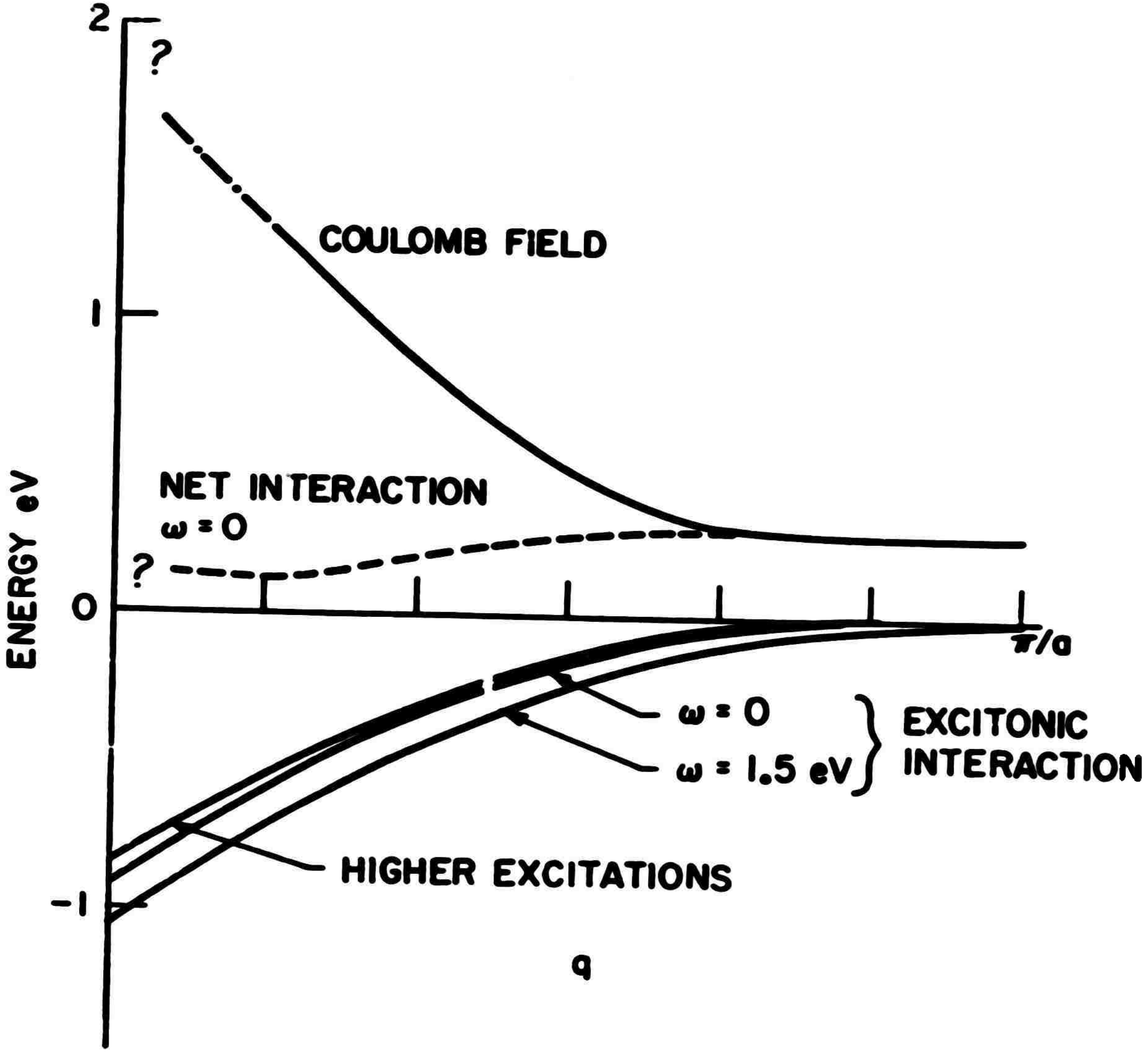


Fig. 3 Computed effective electron-electron interaction due to unscreened Coulomb field, screening due to higher excitations and excitonic term at $\omega = 0$ and $\omega = 1.5$ eV. Wave vector q is along Pt-chain direction.

Thirdly, we see that the higher excitations of the dye weaken significantly the net Coulomb interaction. These dye excitations make the dye array behave as if it were a medium with a dielectric constant of about 2.3.

We are now directing our main effort towards obtaining a reasonable approximation to the screened Coulomb interaction. This is being done by an extention of work originally done by C. G. Kuper (Phys. Rev. 150, 189 (1969)) on single filaments and on filamentary arrays by I. Dzyaloshinsky and E. Kats (JETP 28, 178 (1969)). We plan as a first approximation to use the Thomas-Fermi a proximation to compute the screening.

Band Theory

This phase of the work is proceeding toward calculating wave functions and energy levels describing the electrons in the conducting spine. The states to be described are those whose interactions with the dye molecules will be calculated later using the effective interaction discussed above.

In principle the computation is carried out as an energy band calculation in a metal. Wavefunctions satisfying Bloch's theorem are found for the linear lattice. There are two aspects of this particular system that require special attention. The first is the large number of atoms per unit cell, and the second is the linear nature of the system.

A convenient band theory method for handling many atoms per unit cell is the Green's function method developed by Korringa, and later by Kohn and Rostoker. The dominant feature of the method is the partitioning of space into two regions. The first is the primarily atomic-like region around each nucleus where the potential seen by each electron is assumed to be spherically symmetric, composed of the spherically symmetric potential from the free atom plus the contribution from the other atoms which is spherically symmetric about the atom considered. The second region is the interatomic region in which the potential is simplified to be a constant equal to its average value. The potential here is the self consistent field Hartree-Fock-Slater one electron potential. Wave functions are computed in each region and matched at the boundaries. Care is taken to ensure that Bloch's theorem is satisfied.

Recent work by K. H. Johnson applying the Green's function method to isolated molecules has allowed this calculation to proceed in two steps. Here, the work will proceed first by obtaining wavefunctions for an isolated unit cell; then by modifying these calculations to carry out a full band calculation for the periodic potential.

This latter extension involves the second aspect of the problem referred to above. Since the method used is a Green's function technique, it involves obtaining the value of the wavefunctions at a particular point by integrating over the surface bounding the volume containing the point. In the case of our approximate potential, one obtains the wavefunctions by integrating over the surfaces of all atomic spheres, then demanding continuity of the wave function as the point in consideration approaches one of the spherical surfaces. Integrating over all spheres in the problem thus becomes a sum of contributions from integrals over the linear array of spheres. The primary modification of the first step of the calculation to the second involves these sums. New simplifications in the computation of the these so-called lattice sums have recently been investigated and are being tested in the present systems.

Two computer programs have now been completed to handle the two aspects of the work, and are now being applied to the problem. The purely molecular program has been tested on simple systems and is ready to apply to complex unit cells. The second program, handling the band structure problem is at present being tested on simple model systems.

The Superconducting Gap in a Semiconductor

The Krogmann-type materials appear to be semiconducting rather than metallic so it was thought useful to make some model calculations of the superconducting gap as a function of the magnitude of a semiconductor gap Eg in the energy levels of the electron system. The results obtained give us a rough guide as to the strength of the effective interaction needed to overcome this gap. We find that in the approximation of the model that Eg must be less than $\Delta(o)/2$ where $\Delta(o)$ is the superconducting gap in the absence of a semiconductor gap. This work is discussed below.

The BCS theory of superconductivity gives the following result for the energy gap equation:

$$1 = \frac{V}{2}\sum_k \frac{1}{[e_k^2 + \Delta_o^2]^{1/2}}$$

where $-V<0$ is the attractive pairing potential between two electrons whose energies, e_k, lie below a cutoff frequency, ω_c. Replacing the sum by an integral gives

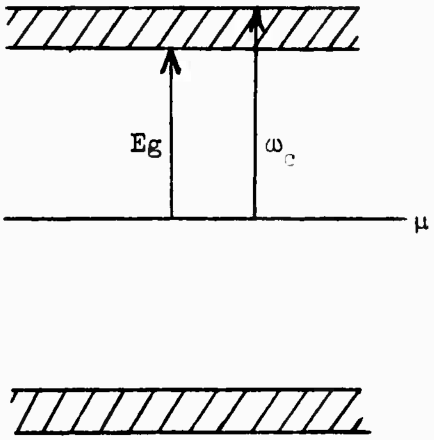
$$1 = V\int_o^{\omega_c} \frac{N(e)\,de}{[e^2 + \Delta_o^2]^{1/2}}$$

In the usual case we assume a constant density of states, N_o, the value at the Fermi level, μ. The consequence is that the superconducting gap is given by

$$\Delta_o = \omega_c/\sinh\left[\frac{1}{N_oV}\right].$$

In order to treat a material with a semiconductor gap extending above and below the Fermi energy by $Eg < \omega_c$ we can assume as a first approximation that the density of states remains constant and all states with $|e_k| < Eg$ are removed.

The range of available states is shown in Fig. 1.



States Available for Pairing
Fig. 4

The energy gap equation becomes

$$1 = N_oV \int_{Eg}^{\omega_c} \frac{d^e}{[e^2 + \Delta_o^2]^{1/2}}$$

whose solution is

$$\Delta_o = [Eg^2 + \omega_c^2 - 2\omega_c Eg \cosh (\frac{1}{N_oV})]^{1/2} / \sinh (\frac{1}{N_oV}) .$$

As a second approximation we can change the density of states to a higher value such that the total number of states remains the same.

$$N_o \longrightarrow N_o \frac{\omega_c}{\omega_c - Eg}$$

The superconductor energy gap becomes

$$\Delta_o = \left\{ Eg^2 + \omega_c^2 - 2\omega_c Eg \cosh \left[\frac{\omega_c - Eg}{\omega_c N_oV} \right]\right\}^{1/2} / \sinh \left[\frac{\omega_c - Eg}{\omega_c N_oV} \right] .$$

The graph shows the superconductor gap as a function of the semiconductor gap; both are given as a fraction of the cutoff frequency.

For $N_oV \gtrsim 1/3$ the superconductor gap is given by

$$\Delta_o = (\Delta^2(o) - 2Eg\Delta(o))^{1/2}$$

where $\Delta(o)$ is the value of the superconductor gap when the semiconductor gap goes to zero. This result follows from the constant density approximation. As the graphs show, as N_oV decreases both approximations give the same result, for Δ_o as a function of Eg. Hence, Eg must be less than $\Delta(o)/2$.

In a different model (W. A. Little, Phys. Rev. <u>A134</u>, 1416 (1964)) where the density of states are peaked at the semiconductor band edge one obtains the condition that Eg must be less than $\Delta(o)$. Thus we expect that in general, the condition would be that Eg must be less than $\alpha\Delta(o)$ where α is a constant of order unity.

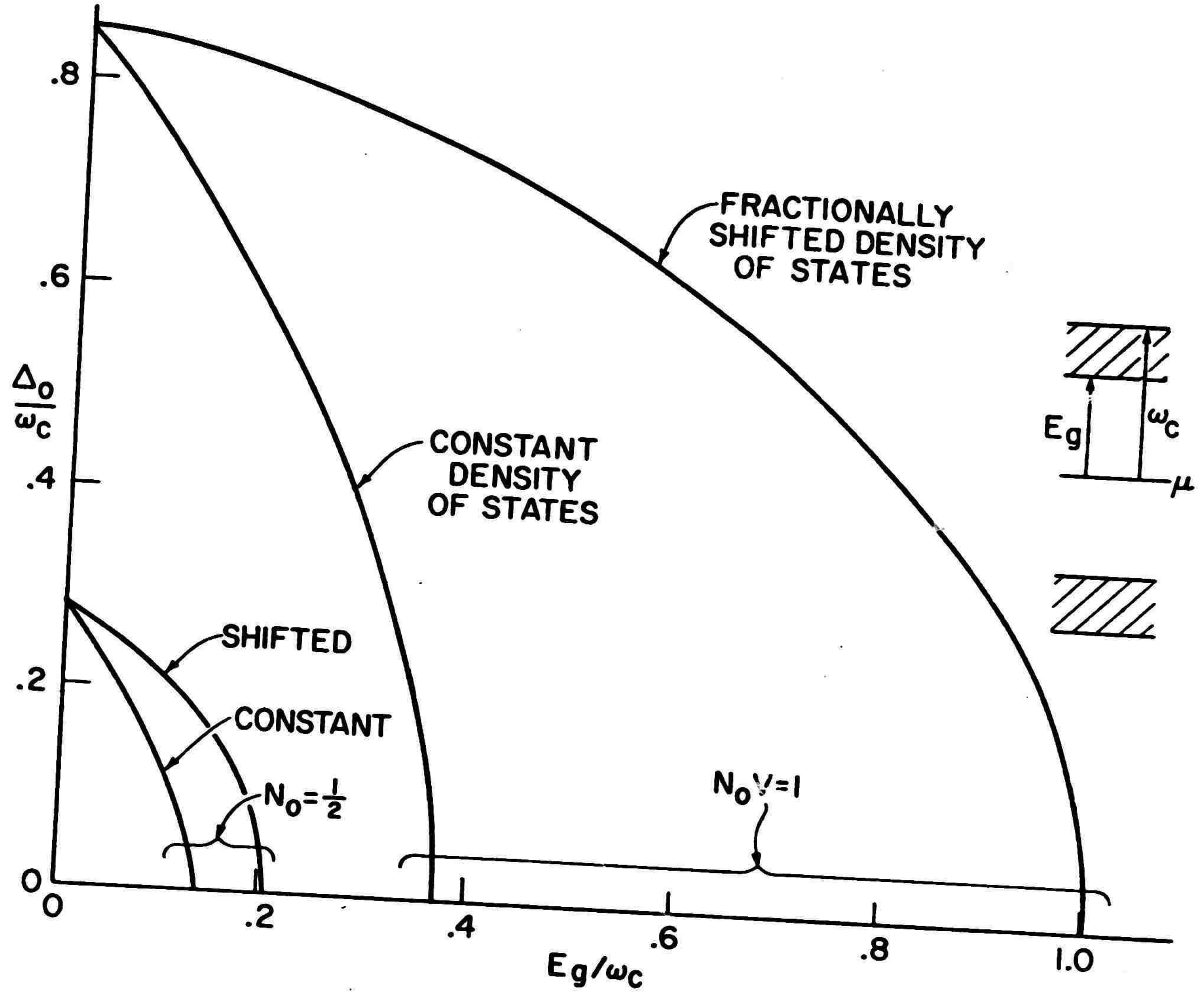


Fig. 5 Superconductor Gap vs. Semiconductor Gap

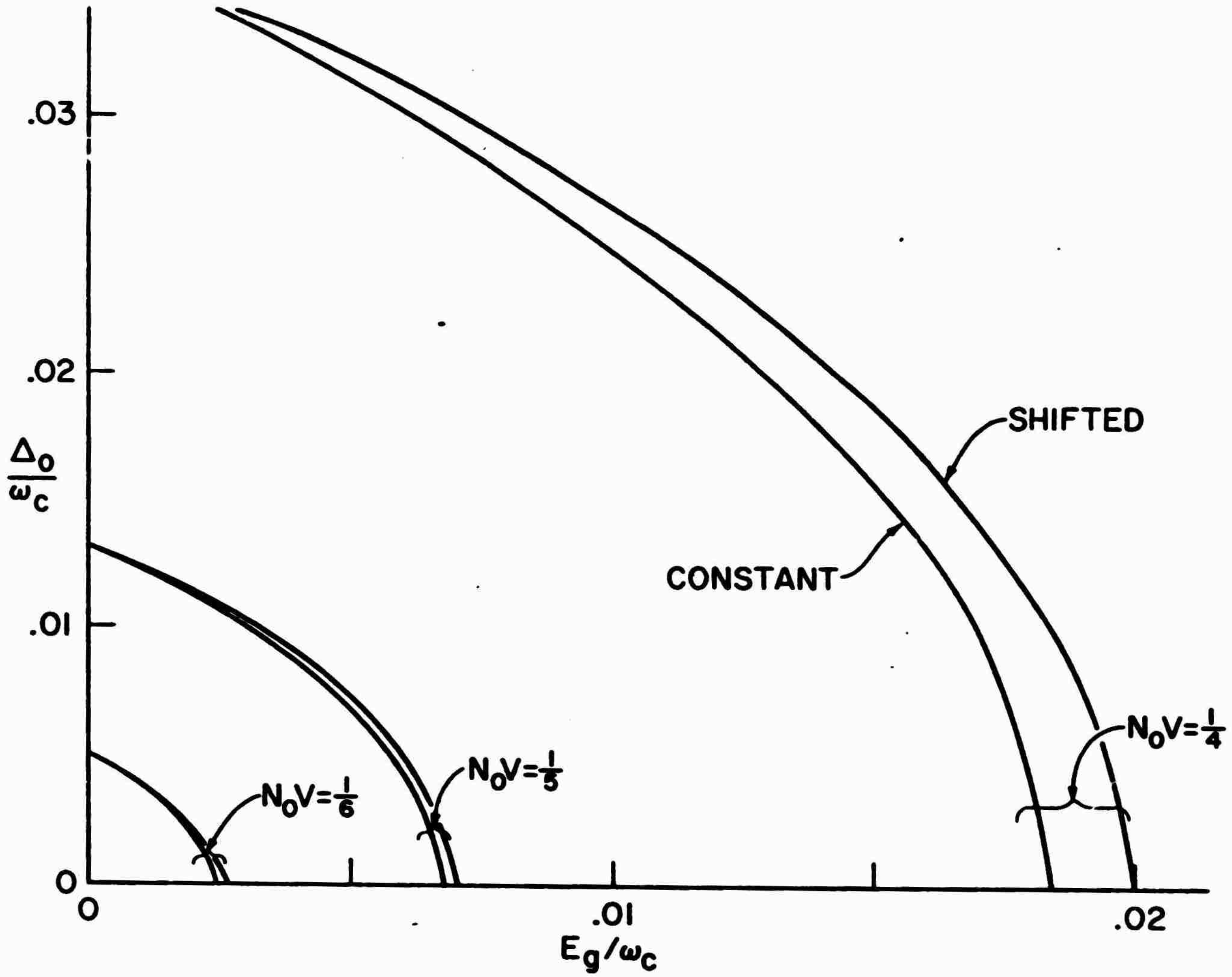


Fig. 5 cont. Superconductor Gap vs. Semiconductor Gap

III. SYNTHETIC PROGRAM

Summary

The synthetic portion of this project is directed towards the preparation of materials to serve as the conducting spine in Little's exiton model. All of our efforts are directed towards substances which have linear chains of covalently bonded metal atoms. Our synthetic efforts can be divided into two portions--the first concerned with materials which have metal-metal bonds or interactions along the principal axis in the crystalline state; and the second materials which are molecular polymers with backbones comprised entirely of covalently bonded metal atoms.

Materials of the first type are easier to prepare and serve as substrates for on going electron transport measurements, providing experimental data which relate to theoretical questions concerning one dimensional conductors. The so-called Krogmann complexes are non-stoichiometric complexes of third row transition elements such as platinum and iridium in which the central metal has on the average an oxidation state corresponding to the electronic configuration $d^{7.7-7.9}$. These materials are characterized by (ca. 2.85 Å) intermetallic distances approximately equivalent to the summation of single bond radii. These substances exhibit high conductivity of the semiconductor type along the intermetallic axis and are characterized by polarized electronic absorption into the far infrared region.

We have been exploring two classes of Krogmann-type, nonstoichiometric compounds--one comprised of anionic metal chains incompassed by ligands such as oxalate or cyanide and surrounded by alkali metal counterions to give electrical neutrality and the other being electrically neutral, having no ionizable anions or cations. The first class is illustrated by $K_{1.64}[Pt(C_2O_4)_2] \cdot H_2O$ and $K_2[Pt(CN)_4Br_{0.30}] \cdot 2.3\,H_2O$. The latter class is illustrated by $Ir(CO)_{2.9}Cl_{1.1}$, and derivatives of this substance in which neutral or anionic ligands have replaced carbon monoxide and chloride respectively. It is now recognized that for our purposes the ionic Krogmann salts have severe disadvantages. Single crystals are difficult to obtain with the exception of the cyanide salt. These ionic crystals are degraded by loss of waters of hydration when placed *in vacuo* or under low humidity. These substances appear to exhibit an ionic as well as an electronic conductivity and in some cases above a certain potential electrolysis of counterions such as bromide is observed. Finally, the chains in these crystalline lattices are tightly bound through ionic coordination such that the introduction of cationic dyes appears to disrupt the crystalline lattice.

It appears that in the case of the molecular Krogmann-type complexes each of these difficulties is obviated. These substances are more amenable to chemical modification and it is hoped that dye molecules can be introduced without disrupting the intermetallic chain. We also intend to prepare molecular nonstoichiometric compounds in which the accompanying ligands are of sufficient girth to separate the metal chains so that we can explore the effect of the intermetallic chain separation on electron screening.

The ionic Krogmann salts are being studied by Dr. Lin. Preliminary exploration of the molecular Krogmann salts has been carried out by Dr. Valentine and will be extended by Mr. MacLaury.

As "frontal assault" on the problem of introducing dyes into linear conductors, Drs. Tammo Winkler and Carl Mayer have explored synthetic routes designed to introduce cyanine dyes into the glyoxime group. If these dye substituted ligands form platinum(II) complexes similar to the simple dialkyl glyoximes, we shall have in hand the first example of an intermetallic chain surrounded by highly polarizable organic molecules. The synthesis of the requisite ligand--dye combination has reached an advanced stage.

Dr. SanFilippo has attempted to develop a selective germanium-germanium coupling reaction. To date, these experiments have been unsuccessful but such explorations will continue inasmuch as chains comprised in part of germanium oligomers are expected to have the desired electrical properties along with high chemical stability.

SanFilippo has also attempted to prepare rhodium analogs of the cobalt co-linear trimetallic monomer, SnCoSn, described in the last report. Using the same uni-valent tetradentate Schiff-base ligand, DOH, SanFilippo attempted to prepare rhodium(III) derivatives. So far these experiments have been unsuccessful but attempts will continue towards this very attractive goal. Such a monomer is expected to have great chemical stability as well as desirable electron transport properties. There seems to be no intrinsic bar to a successful synthesis.

SanFilippo's report contains an account of exploratory studies of quadruple metal-metal bonds involving rhenium, molybdenum, and tungsten. Practical synthetic methods have been developed for the preparation of large quantities of these materials. An interesting side-light of this chemistry is the isomerism arising from the high rotational barrier imposed by the δ bond. As manpower permits, further experiments will be carried out on these quadruple metal-metal bonds in the hope of fashioning a co-linear intermetallic monomer. The question of electron transport through possibly conjugated metal-metal multiple bonds is itself a very interesting theoretical problem. There is to date no reliable model relating the electron transport properties of intermetallic chains with the nature of the bonding and nonbonding orbitals in these chains.

Mr. Murphy's work on this synthesis and polymerization of co-linear trimetallic monomers continues. A new system containing the co-linear arrangement tin-osmium-tin has been prepared. To date, the chemical literature contains no information regarding the synthesis of chemical properties of a tin hydride bearing a transition metal bonded to tin. On the basis of our earlier results, we anticipated that such tin hydride bonds would be very reactive. Murphy's recent work indicates that these bonds are, in fact, quite stable. Working with a model compound, Murphy has been able to isolate and characterize two such substances. He is exploring the coupling reaction of this functional group. Murphy has also uncovered a related coupling reaction in which an osmium hydride reacts with a tin amido derivative affording a tin osmium bond in high yields. This reaction offers the possibility of forming polymers which contain alternating osmium tin bonds. The osmium tin bond is apparently very much stronger than the tin-tin bond. The latter linkage would be present throughout any polymer prepared by the tin hydride coupling reaction. A refined three-dimensional X-ray diffraction study of Murphy's tin-osmium-tin system has been completed by Professor Fleischer. This structure confirms the co-linear arrangement deduced from vibrational spectroscopy. The tin-osmium bond length is considerably shorter than the summation of covalent radii--suggesting the possibility of multiple bonding. It is precisely this type of d-d π-bonding which we expect to transmit the conduction electrons.

PROGRESS REPORT

August, 1971

Doris Lin

During this period, we have continued our studies on the ionic Krogmann compounds. Large, single crystals of the cyano complex, $K_2Pt(CN)_4Cl_{0.3} \cdot 2.6\,H_2O$, have been grown and their crystallographic structure was studied by Professor Fleischer. Electrical conductivity along the metal-metal chain has been measured, and electron probe microanalysis on these crystals has also been carried out. At the same time, in the search for further examples of Krogmann class compounds, we have synthesized and studied a number of square-planar complexes with ligand systems closely resembling the cyano and oxalato ligands in the known partially oxidized Krogmann compounds.

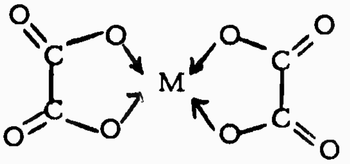
Partially Oxidized Platinum Cyano Compound, $K_2Pt(CN)_4Cl_{0.3} \cdot 2.6H_2O$

This salt was prepared according to Krogmann and Hausen[1]. A solution of $K_2Pt(CN)_4$ (about 16 mmole) was saturated with chlorine, the excess chlorine being boiled off. The resulting solution was heated almost to dryness, whence pale yellow crystals of $K_2Pt(CN)_4Cl_2$ deposited. This was to make sure that the dichloro compound was the only product formed. Slow evaporation of an aqueous solution containing the complex salts $K_2Pt(CN)_4Cl_2$ and $K_2Pt(CN)_4$ in a molar ratio of 1:5 gave needles with a coppery sheen and having the composition $K_2Pt(CN)_4Cl_{0.3} \cdot 2.6H_2O$.

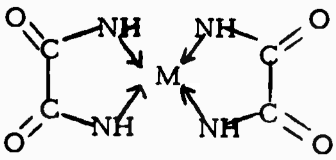
Crystals of these cyano compounds were much larger than the corresponding partially oxidized oxalato compounds which we previously reported[2]. They were usually of the dimension 2 x 0.1 x 0.1 mm. Larger crystals (up to 2 x 1 x 1 mm) were obtained by setting the aqueous solution containing the crude product aside for several weeks. Conductivity measurements along the other two dimensions of the crystals are currently being carried out. X-ray crystallographic studies have been done by Professor Fleischer, and the Pt-Pt distance was found to be 2·88A.

During the course of electrical conductivity measurements on single crystals of $K_2Pt(CN)_4Cl_{0.3} \cdot 2.6H_2O$, we have observed an oxidation-reduction reaction. After the application of a D.C. voltage of >6 volts to the crystal, there was a color change at the anode end of the crystal, from the metallic copper color of the original compound to a greyish-white color with no metallic luster. Electron probe microanalysis shows that in the original crystal, $K_2Pt(CN)_4Cl_{0.3} \cdot 2.6H_2O$, the K^+ and Cl^- contents are constants throughout the whole length of the crystal, corresponding to 18% K^+ and 2.5% Cl^-, in excellent agreement with the results obtained by chemical microanalysis. However, the greyish-white end of the crystal has a much lower Cl^- content than that of the original compound, while the K^+ content remains the same (18%) throughout the entire crystal. At present, we are growing bigger single crystals of the oxalato complex, $K_{1.6}Pt(C_2O_4)_2$ and a similar study will be carried out to see if the K^+ content changes after the application of a D.C. voltage. This would enable us to draw a conclusion as to the mechanism for the reported reaction.

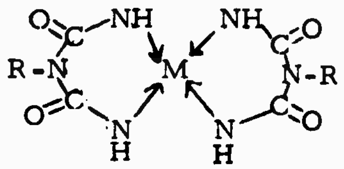
Copper (III) and Nickel (III) Complexes of Biuret and Oxamide



(a) Oxalato complex



(b) Oxamidato complex



R=H, n-propyl, phenyl, or dye.

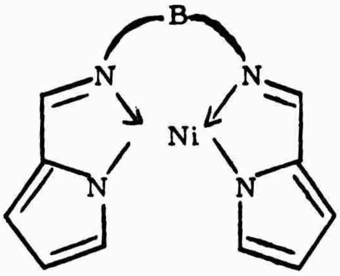
(c) biuretato complex

The oxamid and biuret ligand systems closely resemble the oxalate ones found in the Krogmann complexes (see figs. a, b, and c). They form complexes of Cu(II) and Ni(II), with the compositions of $K_2Cu(bi)_2$, $K_2Ni(bi)_2$ and $K_2Cu(oxam)_2$, which can further be oxidized by $K_2S_2O_8$ to give deeply-colored, highly insoluble square-planar complexes $KCu(bi)_2$, $KNi(bi)_2$ and $KCu(oxam)_2$ respectively[3].

We prepared the biuret complexes; $KCu(bi)_2$ was dark brown and $KNi(bi)_2$ was blue-black. The electrical conductivity of a powder pellet of $KNi(bi)_2$ at room temperature was found to be $\sim 10^{-9}$ $ohm^{-1}cm^{-1}$. However, the extremely low solubility of the salts hamper further study. We are now currently preparing analogous complexes derived from the alkyl-substituted biuretate ions (of the type HNCONRCONH) which are soluble in acetone, alcohol and DMSO with the hope of attaching a dye molecule in the ligand system eventually.

Nickel Complexes Derived from Pyrrole-2-carbaldehyde and Aliphatic and Aromatic Diamines.

It was reported[4] that diamines react with two moles of pyrrole-2-carbaldehyde giving potential chelating ligands containing four nitrogen donor atoms, two of which each carry a labile proton. Deprotonation of these ligands in the presence of Ni^{2+} ions gave square-planar complexes (see Fig. d). By changing the bridging group B, the size and nature of the central chelate ring of the tricyclic ligand system can be varried.



(fig. d)

We have successfully prepared the complexes of Ni(II) with B=1,2-diaminoethane and 1,2-diaminobenzene. Both complexes are nice crystalline compounds, being brick-red and dark-red in color respectively. Further work has to be done along this series, and we plan to synthesize the corresponding complexes of Pd(II) and Pt(II) as an initial step of preparing potential Krogmann class compounds.

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THE SYNTHESIS OF STACKED SQUARE-PLANAR IRIDIUM COMPLEXES

August, 1971
Joan Valentine

Introduction

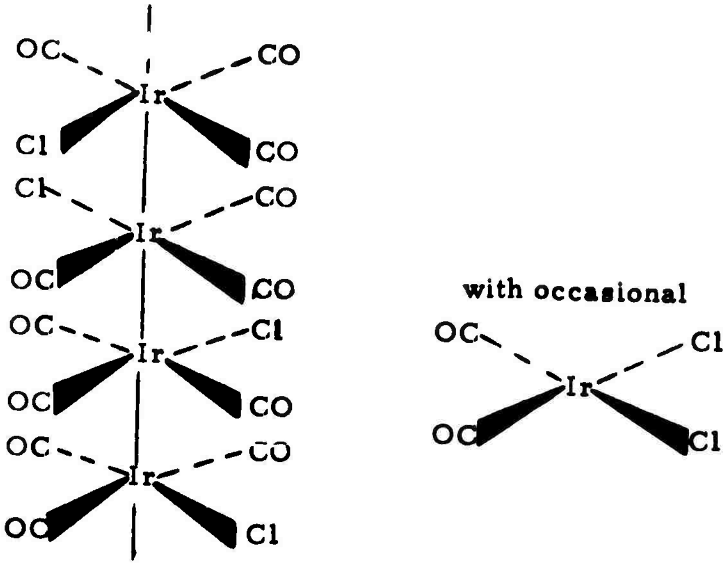
This report deals with attempts to prepare neutral iridium complexes which exist in crystal forms as columnar stacks of metal atoms with strong metal-metal interactions. Recently anisotropic semiconducting properties along the long axis of crystals of such materials have been demonstrated.[1-5]

The model complex for such preparations is "$Ir(CO)_3Cl$" which has recently been reassigned the stoichiometry $Ir(CO)_{2.9}Cl_{1.1}$.[6]

This complex is thought to exist as a long chain of stacked square planar $Ir(CO)_3Cl$ groups with occasional $Ir(CO)_2Cl_2$ groups (see Figure 1)[6]. The short metal-metal distance (2.85 Å) indicates a bonding metal-metal interaction. This can be contrasted with the stacked complex $Ir(CO)_2$(acac) where the Ir-Ir distance is 3.20 Å.[1] Room temperature conductivity of "$Ir(CO)_3Cl$" has been measured as 10^{-2} ohm^{-1} cm^{-1} along the needle axis.[7] Unfortunately this complex is totally insoluble and thus large crystals cannot be grown. Moreover there is no way to introduce dyes into the crystal to test their effect on conduction properties as predicted by Little's theory.[8]

The synthetic approach to developing complexes analogous to "$Ir(CO)_3Cl$" has been: 1) reaction of "$Ir(CO)_3Cl$" with chlorine in the hope that a different $Ir(CO)_xCl_y$ might be soluble, 2) reaction of "$Ir(CO)_3Cl$" with p-toluidine to form "$Ir(CO)_3LCl$" in the hope that this might exist in a nonstoichiometric form and thus allow an attachment

FIGURE 1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Ir
OC
Cl

point for dyes and 3) reaction of $Ir(CO)_2(acac)$ with small amounts of chlorine in the hope that chlorine atoms will substitute for CO in a partially oxidized form.[9]

Experimental[*]

All reactions were carried out under argon in dry solvents deaerated with a stream of argon. Infrared spectra were obtained in KBr pellets on a Perkin-Elmer-457 Grating Infrared spectrophotometer. Elemental analyses were performed by the Stanford Microanalytical Laboratory. Iridium trichloride, $IrCl_3 \cdot 4H_2O$(52.00% Ir), was obtained from Mathey Bishop. $IrBr_3 \cdot 4H_2O$ (38.33% Ir) and K_2IrCl_6 (41.08% Ir) were obtained from Engelhard. 3-Methylacetylacetone was obtained from K + K Laboratories. p-Toluidine was obtained from Aldrich. Cyclooctene was purified by passage through silica gel. Chloro-bis-cycloocteneiridium dimer, $Ir_2(cyclo\text{-}C_8H_{14})_4Cl_2$, was prepared (p53) as follows: Cyclooctene (8 ml), isopropyl alcohol (20 ml) and distilled water (60 ml) were deaerated with a stream of argon. K_2IrCl_6(4.4g) was added and the mixture was refluxed with vigorous stirring under argon for 2 - 3 hours until the brown solution had become a pale green solution mixed with an orange-yellow oil. The mixture was cooled to 20° C and the solution decanted from the oil. The oil was crystallized by trituration with deaerated ethanol, filtered, washed with ethanol, and dried in vacuum. Yield: 3g (75%).

"Chlorotricarbonyliridium",[10, 11] $Ir(CO)_3Cl$ or $Ir(CO)_{2.9}Cl_{1.1}$, (p. 1-4, 16)

Iridium trichloride, $IrCl_3 \cdot 4H_2O$, (2.0g) dissolved in 15 ml H_2O was mixed with 15 g silica gel (40 - 140 mesh) and dried overnight in a vacuum oven at 120° C. The silica gel mixture was placed between two glass wool plugs with a thermometer inserted in it in a 20 x 500 cm pyrex tube. Chlorine gas was passed through and the tube heated to

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[*] Page numbers in parentheses refer to research notebook.

150°C in a tube furnace until no water condensed in the cool end of the tube (1/2 - 2 hours). The water was wiped off periodically. The gas was changed to CO and the temperature raised to 180°C. Within an hour a copper-colored metallic material had started to condense in the cool portion of the tube. Over a period of several days a material resembling dirty glass wool deposited in the tube. This was scraped out several times during the reaction. Yield varied from 20 to 80 percent. Control of the temperature appeared to be crucial. Regeneration of the silica gel by passage of chlorine at 150°C once a day appeared to increase the rate of condensation but not necessarily the yield. The material thus obtained was used as a starting material in further reactions even if contaminated by silica gel. The material could be resublimed in a stream of CO at 180°C. The best crystals obtained in all cases appeared under magnification to be bunches of hair-like needles. I.R.: 2070(s), 573(w), 507(s), 465(s), 380(w), 320(w); broad absorption 4000 - 800 cm^{-1}.

The material appears to be totally insoluble in noncoordinating solvents. In chlorobenzene at 190°C under 40 lbs of CO, the material appeared to dissolve but upon cooling, the material was a very fine black powder whose infrared spectrum showed some decomposition.

When "$Ir(CO)_3Cl$" is needed as a starting material (see below), a much more easily obtained and cheaper starting material is preferred (p. 51, 54). $Ir_2(cyclo\text{-}C_8H_{14})_4Cl_2$ was suspended in hexane ($\sim$1 mg/ml). CO was bubbled through the solution until all the starting material had been converted to a black precipitate and the solution was nearly colorless. This material was filtered immediately washed 5 times with hexane, and dried quickly with a stream of argon. The product, a black-red shiny powder (0.5 mg per mg starting material) has an infrared similar to "$Ir(CO)_3Cl$". I.R.: 2140(w), 2070(s), 573(w), 507(s), 465(s), 380(w), 320(w), broad absorption 4000-800 cm^{-1}. Analysis (JV-23): Found C, 10.70; H, 0.41; Cl, 10.64; Ir, 60.79. Calculated for $Ir(CO)_3Cl$ C, 11.5; H, 0.0; Cl, 11.4; Ir, 61.4.

This material <u>must</u> be used at once for further reaction. It appeared to decompose in 24 hours under vacuum to a material that absorbed throughout the infrared with a featureless spectrum and which reacted only slightly with 3-methylacetylacetone to give $Ir(CO)_2$(3-Me acac). Freshly prepared material reacted with acetylacetone and p-toluidine to give the desired complexes in approximately one-tenth of the time required for the material produced by the silica gel method (see below).

'Bromotricarbonyliridium", [10] $Ir(CO)_3Br$? (p. 34-35).

Preparation of bromotricarbonyliridium using $IrBr_3 \cdot 4H_2O$ was analogous to that of the chloro complex. $IrBr_3 \cdot 4H_2O$ (2 g) dissolved in 150 ml water was mixed with 25 g silica gel and dried in a vacuum oven at 85°C overnight. HBr was used in place of chlorine to dry the silica gel mixture. In 2 - 3 days, 600 mg (60%) of product identical in appearance to the chloro analogue had condensed in the tube. The product was resublimed at 160° C in a stream of CO. I.R.: 2080(s), 580(w), 495(s), 463(s), 385(w), broad absorption 4000 - 1200 cm^{-1}. Analysis (JV-2): calculated for $Ir(CO)_3Br$, C, 10.01; H, 0.0; Br, 22.4; Ir, 54.0. Found C, 10.11; H, 0.0; Br, 23.73; Ir, 51.68.

The yellow material left behind in the silica gel is soluble in THF. This material which may be $Ir(CO)_2Br_2$ referred to in ref. 10 was not isolated.

2,4-Pentanedionatodicarbonyliridium[1], $Ir(CO)_2$(acac) (p. 14-15, 32, 50)

"Chlorotricarbonyliridium", "$Ir(CO)_3Cl$", (obtained by the silica gel method, 480 mg), $NaHCO_3$ (630 mg), and acetylacetone (0.21 ml) in 200 ml benzene were refluxed with vigorous stirring for 4 days. The solution was cooled to 20°C, filtered and evaporated to approximately 5 ml under reduced pressure. The solution was refrigerated overnight and the gold crystals filtered. Further evaporation and cooling produced a second crop. Yield 440 mg (81 %). This material could be purified further by sublimation at 75°C (0.5 mm Hg). I.R.: 2045(s), 1975(s), 1520(m), 1360(m), 1280(w), 1199(w), 1020(w), 930(w), 790(w), 660(w), 620(w), 595 (w), 460(w), 413(w) cm^{-1}. The initial, sublimed material is blue but gives an infrared spectrum identical to the yellow material sublimed later. This may be due to the crystal form since the yellow crystals are strongly dichroic, yellow down the short axes and blue-black down the long axis, but it may also be due to traces of an impurity such as chlorine.

The reaction time is reduced to approximately 4 hours when freshly prepared iridium carbonyl chloride made from the chlorocyclooctene dimer is used. In both cases, the endpoint of the reaction is variable. Best results were obtained by allowing the reaction to continue until most of the insoluble material was gone. The endpoint was deceptive since there are varying amounts of an insoluble blue byproduct formed. I.R. 1610 (broad), 1450, 1400-1250 (broad), 1030, 990, 835, 690, 665 cm^{-1}.

3-Methyl-2,4-pentanedionatodicarbonyliridium, $Ir(CO)_2(3\text{-}Me\ acac)$ (p. 43-44, 48-49).

The 3-methylacetylacetone derivative was prepared by the analogous method. "Chlorotricarbonyliridium", "$Ir(CO)_3Cl$", from the silica gel preparation (500 mg), $NaHCO_3$ (550 mg) and 3-methylacetylacetone (0.25 ml) in 150 ml benzene were refluxed for 4 days. Yield: 490 mg (89%) of orange-yellow crystals. The endpoint of this reaction is also deceptive due to the presence of a soluble green contaminant and a black insoluble byproduct. The green contaminant sublimes with the product but can be removed by recrystallization from acetone. Analysis was carried out on sublimed material which contained some green material. Anal: (JV-8) Calcd for $Ir\ C_8H_9O_4$; C, 26.5; H, 2.48; Ir, 53.2; mw 361. Found C, 26.39; H, 2.38; Cl, < 0.05; Ir > 51.5; mw 362. The infrared showed carbonyl peaks at 2050 and 1970 cm^{-1}.

Crystals of both compounds can be grown by slow cooling of a warm acetone solution in a dewar of warm water (p. 17). Care must be exercised that air is excluded and that the solution is not left at the boiling point for long. Both complexes have been observed to decompose in boiling acetone solution over several hours. Crystals of the acetylacetone complex are oblong and very metallic in appearance, resembling chunks of gold metal. Crystals of the 3-methylacetylacetone complex are yellow needles.

Chlorodicarbonyl-p-toluidinoiridium, $Ir(CO)_2(NH_2C_6H_4CH_3)(Cl)$ [12,13] (p. 32, 46, 54).

"$Ir(CO)_3Cl$" prepared by the silica gel method (200 mg) and p-toluidine (83 mg) were refluxed in benzene for 24 hours. The solution was cooled to 20 °C, filtered, and evaporated under reduced pressure. The blue powder was sublimed (110° C, 2 mm) to give 180 mg of blue powder. I. R.: 2083(s), 2043 (m), 2020 (s), 1970 (w), 1505 (m), 1140 (w), 1117(m), 820(m), 700(w), 640(w), 565(w), 515(m) cm^{-1}. Anal (JV-6): Calculated for Ir $C_9H_9NO_2Cl$ C, 27.6; H, 2.30; N, 3.58; Cl, 9.08; Ir, 49.1. Found C, 28.23; H, 2.39; N, 3.51; Cl, 9.61; Ir, 47.6.

The reaction with starting material obtained from the chloro cyclooctene iridium dimer was complete in 2 1/2 hours. The yield was lower than the reaction preceeding but this is probably because the starting material was partially decomposed.

The non-volatile material left in the sublimator from this reaction absorbs in the infrared with broad absorption 4000-400 cm^{-1} with a small carbonyl peak at 2040 cm^{-1}. A pressed pellet of this material had a conductivity comparable to that of "$Ir(CO)_3Cl$". It has not yet been further characterized.

Long blue-red needles of metallic appearance were obtained by slow cooling of a benzene solution of $Ir(CO)_2$(p- toluidine)Cl under argon. Solutions of this material maintained near the boiling point for several hours also began to decompose.

Reaction of $Ir(CO)_2$(acac) and $Ir(CO)_2$(3Me-acac) with chlorine (p. 24, 29-31, 37-39, 47-49).

$Ir(CO)_2$(acac) (276 mg) was dissolved in 40 ml benzene in a Schlenk tube capped with a rubber septum cap under argon. Chlorine gas was injected in approximately 2 ml aliquots. The yellow solution became red then brown and a black precipitate formed. The solution was filtered under argon and more chlorine added. The process was repeated until no precipitate formed after a total addition of 12 ml of Cl_2. The yellow solution remaining was evaporated to give a yellow oil which crystallized upon cooling and trituration with methanol. The infrared spectrum showed at least 4 carbonyl or hydride bands in the region 1980 - 2100 cm^{-1} and no absorption in the 1500 cm^{-1} region. Other preparations gave different yellow products with several carbonyl or hydride bonds at 2080-2160 cm^{-1}.

Infrared spectra of samples 1 - 5 (186 mg) were similar and these were combined. I.R.: broad absorption 4000 - 800 cm^{-1}, carbonyl band 2060 cm^{-1}, weak band at 550 cm^{-1}. Sample 6 (17 mg) did not have a carbonyl band in the infrared although it also showed broad absorption. Recrystallization of 50 mg of the combined samples by dissolving in 120 ml THF, producing a yellow solution, evaporation under reduced pressure to 30 ml when the solution was blue and crystallization began, and cooling gave 13 mg of black shiny powder. I.R.: broad absorption 4000-250 cm^{-1}, 2050 (w), 550 (w). Analysis (JV-7): Found: C, 17.38; H, 1.75; Cl, 10.87; Ir, 53.8. Material prepared similarly in CH_2Cl_2 and not recrystallized gave the following analysis (JV-1) Found: C, 19.89; H, 1.65; Cl, 7.13. Material prepared similarly in benzene and recrystallized from THF gave the following analysis (JV-3): C, 18.92; H, 1.89; Cl, ~ 10.3; Ir ~ 50.6.

Attempted recrystallization from warm acetone resulted in decomposed material: a yellow powder and brown solution.

The combined fractions 1 - 5 appeared to sublime at 140 - 150°C (~ 1 mm Hg), although it is possible that the material was decomposing to give this volatile fraction. The sublimed product was a small amount of red-blue powder whose yield was similar to that obtained by recrystallization. I.R.: broad absorption 4000 - 400 cm^{-1}, 2050 (m), 630 - 600 (w), 550 - 500(m). Analysis (JV-7s) Found: C, 17.75; H, 1.19; Cl, 7.72; Ir, 52.84. Some starting material, $Ir(CO)_2(acac)$, sublimed to the top of the probe and a brown residue (not strongly absorbing in the infrared) was left after the sublimation.

The presence of hydride peaks in the byproducts of this reaction and the lack of stability of reaction solutions suggests that some HCl is being formed by chlorination of the acetylacetone ring. To eliminate this possibility the 3-methylacetylacetone complex was chlorinated.

The 3-methylacetylacetone complex, $Ir(CO)_2(3Me\text{-}acac)$, (50 mg) in benzene solution was reacted with chlorine by injection of a small amount (<1 ml) of chlorine saturated benzene. The solution turned vivid shades of red and a brown precipitate formed. This material (50 mg) was filtered and sublimed at 180°C giving starting material, brown residue, and 8 mg of product. Possibly this is a decomposition product. I.R.: broad absorption 4000 - 250 cm^{-1}, 2060 (m), 550(w), 500(w), 445(w). Analysis (JV-20) Found: C, 20.34; H, 1.98; Cl, 6.26; Ir, 55.69.

Reaction of $Ir(CO)_2(acac)$ with N-chlorosuccinimide gave green, unstable solutions which upon evaporation gave infrared spectra indicating hydride formation presumably from HCl.

Reaction of "$Ir(CO)_3Cl$" with chlorine (P. 25-27, 32, 33).

"Chlorotricarbonyliridium", "$Ir(CO)_3Cl$" (200 mg) from the silica gel preparation was suspended in 25 ml CH_2Cl_2 in a Schlenk tube. This mixture was deaerated with argon and saturated with Cl_2. This mixture was stirred vigorously for 24 hours with periodic resaturation with Cl_2. The reaction vessel when opened gave off clouds of white vapors, probably $COCl_2$. This mixture was evaporated to give a yellow powder and, taking great care not to contaminate with air, transferred to a vacuum dessicator overnight. The resulting brown powder was treated with 5 ml of deaerated reagent grade chloroform. The brown precipitate (80 mg) was filtered. Recrystallization by evaporation under reduced pressure of a solution of the product in acetone followed by cooling gave 21 mg of a coppery powder. The acetone solution was yellow when dilute and deep blue when concentrated. I.R.: broad absorption 4000 - 300 cm^{-1}, 500 cm^{-1} (w). Analysis (JV-5): C, 6.86; H, 0.75; Cl, 17.02; Ir, 53.3. After reprecipitation from acetone by addition of benzene, the analysis (JV-5r) was Found: C, 8.16; H, traces; Cl, 16.08; Ir, 55.43.

Reaction of $Ir_2(cyclo\text{-}C_8H_{14})_4Cl_2$ with CO in acetone

Chloro-bis-cycloocteneiridium dimer, $Ir_2(cyclo\text{-}C_8H_{14})_4Cl_2$, (100 mg) in 10 ml of acetone was reacted with a stream of CO until the solution was blue and all starting material was consumer ($<$ 1 min). This solution stood for several minutes until a yellow powder had precipitated. This was filtered and the blue solution was evaporated under reduced pressure to a copper-gold powder. The cyclooctene was removed by several washings with hexane. The yellow powder was identified as $Ir_4(CO)_{12}$ by its infrared spectrum (2100 - 1975 (s), 540(s), 500(s), 475(m), 443(s)cm^{-1}). The coppery powder was recrystallized from acetone by dissolving, evaporating under reduced pressure, and cooling. Analysis (JV-21) Found: C, 10.95; H, 1.17; Cl, 13.46; Ir, 56.5. I.R.: broad absorption 4000 - 250 cm^{-1}. The analysis indicates acetone or a product of acetone has been incorporated in the product.

When a blue solution of product and cyclooctene was warmed and allowed to stand overnight, the product was yellow crystals whose infrared spectrum indicated a cyclooctene complex.

When the reaction of cyclooctene chloroiridium dimer with CO was carried out in dilute solution, the initial solution color upon addition of CO was green and a black precipitate ("$Ir(CO)_3Cl$"?) resulted. Purging of this solution with argon resulted in a blue solution with no precipitate. Addition of CO regenerated the green solution plus precipitate. No formation of $Ir_4(CO)_{12}$ was observed and evaporation of the blue solution gave a brown oil. Presumably the reaction must be carried out rapidly and/or in concentrated solution to prevent reaction of the desired product with cyclooctene.

Results and discussion

The purpose of this project is the preparation of neutral complexes with chains of stacked iridium atoms with the requirement that they be soluble so that crystals suitable for physical measurements can be grown.

Three stoichiometric complexes were prepared, two of which were previously known: $Ir(CO)_2(acac)$[1], $Ir(CO)_2(3\text{-Me acac})$, $Ir(CO)_2$(p-toluidine)Cl[12,13]. Crystals of the first and last complex were prepared and physical measurements are in progress. The properties of the 3-methylacetylacetone derivative may be interesting since crystals of the complex lack the characteristic metallic appearance of the other two. Crystals of this complex will be prepared soon so that these measurements may be made. Preliminary single crystal studies of the other two complexes indicate that they are semiconductors down the long axis. Further studies are in progress in the physics group.

Crystals of two previously known halotricarbonyl iridium complexes were prepared, "$Ir(CO)_3Cl$,"[10,11] and "$Ir(CO)_3Br$"[10]. The stoichiometry of the first complex is thought to be $Ir(CO)_{2.9}Cl_{1.1}$; the exact stoichiometry of the bromo complex has not yet been investigated. The metallic appearance of the two complexes, the lack of solubility, the air stability, and the short metal-metal distance (2.85 Å) of the chloro complex and its high conductivity in pressed pellet form support Krogmann's suggestion that the complex is nonstoichiometric.

The crystal form of the two complexes is bunches of very fine hairlike needles. This form is unsuitable for good physical measurements. Unfortunately, these complexes which have very strong attractive interactions along the long axis and weak forces laterally tend to form very fine long hairs. It is possible that sublimation of these complexes in a stream of CO to a heated probe would cause slower condensation and larger crystals. It is also possible that slow addition of CO to a solution of the cyclooctene chloro iridium dimer, $Ir_2(cyclo\text{-}C_8H_{14})_4Cl_2$ would result in thicker crystals, if this complex is indeed the same as the product formed from $IrCl_3$ on silica gel.

Comparison of the properties of "$Ir(CO)_3Cl$", "$Ir(CO)_3Br$", and "$Ir(CO)_3I$",[10] a careful study of their stoichiometries, and measurement of the metal-metal separation by x-ray diffraction should be very interesting. The substitution of Cl by Br and I should affect the material both electronically and sterically.

Attempts at preparation of soluble neutral non-stoichiometric complexes have resulted in five materials which have properties expected for such complexes by analogy with ionic nonstoichiometric platinum complexes[9]: 1) broad absorption of the solid in the infrared region, 2) non-Beer's law behavior in solution, 3) metallic appearance in the solid, 4) good conduction properties in pressed pellet form.

Five materials prepared display some or all of these properties. The preparations and properties are summarized in Table 1.

Unfortunately, these complexes have not yet been fully characterized. If they are non-stoichiometric, it is impossible to tell from analysis if the complex has been successfully purified except by many repeated preparations and purifications giving consistent analyses. It is also possible that these complexes do not represent sharp minima but that the ratio of, for example, chloride to iridium and thus the oxidation state of iridium can vary. This type of behavior has been observed by Malatesta and Canziani[14] who, in attempting to prepare the chloro analogue of $K_2[Ir_2(CO)_4Br_5]$, obtained $K_2[Ir(CO)_4Cl_{4.5-4.8}]$. Speculation about the stoichiometries of these complexes is difficult since consistent analyses have not been obtained. This must await further characterization of these complexes.

TABLE 1

Preparation	IR	Solid Appearance	Conductance in Pressed Pellet	Solution Behavior		Comments on Stoichiometry
				dilute	concentrated	
1) "$Ir(CO)_3Cl$" + Cl_2	broad absorption 4000 - 300 cm^{-1}	metallic	not measured	yellow	blue	$Ir(CO)_aCl_b$ inconsistent results
2) $Ir_2(cyclo\text{-}C_8H_{14})_4Cl_2$ + CO + acetone	broad absorption 4000 - 250 cm^{-1}	metallic	comparable to "$Ir(CO)_3Cl$"	yellow	blue	$Ir(CO)_cCl_d(acetone)_e$ analysis indicates presence of H
3) $Ir(acac)(CO)_2 + Cl_2$	broad absorption 4000 - 400 cm^{-1}	metallic(?) flakes or black shiny powder	not measured	yellow	blue	$Ir(CO)_fCl_g(acac)_h$ acac ring may be chlorinated
4) $Ir(Me\text{-}acac)(CO)_2 + Cl_2$	broad absorption 4000 - 250 cm^{-1}	metallic(?) flakes or black shiny powder	not measured	yellow	blue	$Ir(CO)_iCl_j(Meacac)$,
5) "$Ir(CO)_3Cl$" + p-toluidine byproduct	broad absorption 4000 - 400 cm^{-1}	black powder	comparable to "$Ir(CO)_3Cl$"	not observed		?

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Suggestions for future experiments

1. a) Make $Ir(CO)_3I$
   b) Compare physical properties of $Ir(CO)_3X$
   c) Three ways to try to grow crystals are sublimation to a heated probe, slow reaction of CO with the chlorocycloocteneiridium dimer, and dissolving $Ir(CO)_3Cl$ under pressure of C_2H_4.
   d) Check if material made from chlorocycloocteneiridium dimer sublimes in CO at 180°C.

2. Grow crystals of acac complexes for physics.

3. Investigate black byproduct of $Ir(CO)_2$(p-toluidine)Cl preparation. Try reacting $Ir(CO)_2$(p-toluidine)Cl with small amount Cl_2.

4. Make the 4 possibly non-stoichiometric complexes and purify until consistent analytical results are obtained. Atomic absorption spectroscopy may be useful to get exact metal-to-chlorine ratios. The mass spectroscopy of these complexes might be interesting since some of them at least sublime. Grow crystals.

5. It would be interesting to study the visible spectrum of one of the non-Beer's law complexes as a function of concentration. A very thin cell would be necessary.

6. Investigate the possibility that the product of reaction of $Ir_2(cyclo\text{-}C_8H_{14})_4Cl_2$ with CO in acetone reacts reversibly with CO.

7. a) $Ir(CO)_3Cl$ + orthochloranil, $C_6Cl_4O_2$?
   b) $Rh(CO)_2$(acac) + Cl_2 ?
   c) $Ir(CO)_3Br + Br_2$?

8. The product of $Ir(CO)_2(acac)$ + Cl_2 may leave chlorinated acac. Can degrade and complex with Cu to identify.

9. $Ir(CO)_2Cl_2^-$ + acac?
   + CO ?

Dye-substituted Glyoxime-d^8-metal-Complexes
Model of a High Temperature Superconductor

C. Mayer and T. Winkler

I. Introduction

This report reviews the continuation of the synthetic experimental work in connection with the formation of a model compound for Little's theory[1] of a high temperature superconductor, formerly reported to the Bonneville Power Administration.[2]

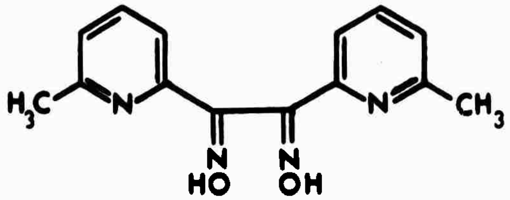
As a model compound we chose a dye substituted d^8-metal-glyoxime complex. The reason for this choice and the expected properties of the system are extensively described in Appendix A.

Section II of this report deals with further attempts to find a way to resolve the quarternization problems formerly reported.[2] Section III gives the first results on a modified glyoxime system. Section IV covers experimental data and section V a few related experiments.

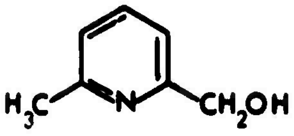
II. Dye substituted picolil dioxime derivative

The difficulties reported formerly[2] to quarternize compound I

I



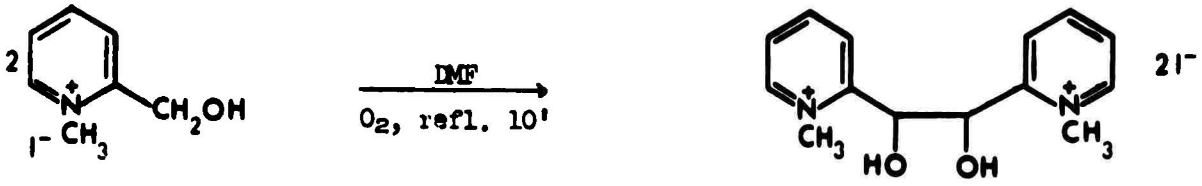
as a necessary step to perform cyanine dye chemistry on this system made it urgent to find another way to obtain that compound. Since it was known that compound II



II

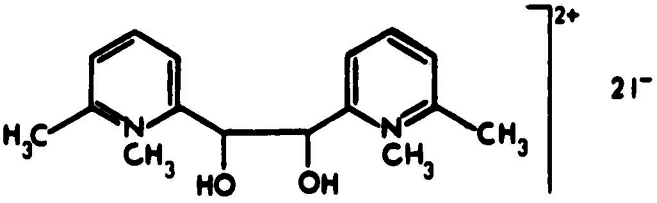
was easily quarternized, the following reaction reported in the literature[3] seemed to be feasible, provided one of the very few methods to oxidize vic-glycols without cleavage would work.

Reported case:



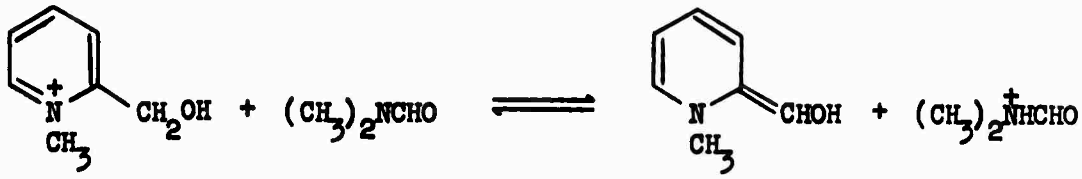
III

In our case, instead of using pyridyl-2-carbinol, we had to start with 6-methyl-pyridyl-2-carbinol to obtain glycol IIIa.



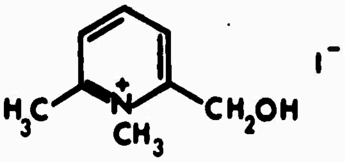
IIIa

Unexpectedly, this oxidative coupling reaction failed with that educt. At first, even the reproduction of the results from the literature gave some difficulties. The reason for the initial failure of those experiments was the fact that we used highly purified dimethylformamide which contained no dimethylamine. Whereas the authors claimed DMF to act as base, i.e.



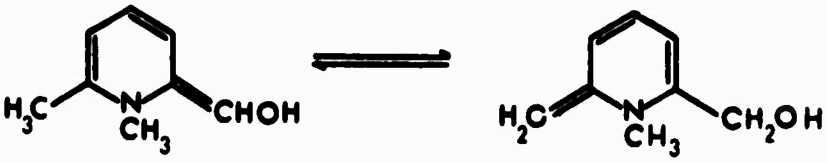
we found that this is not the case. On using reagent grade DMF which normally contains traces of dimethylamine the reaction occurred smoothly. Also with the highly purified DMF, after addition of some of the amine, the reaction worked. Reaction time necessary and yield vary greatly with the amount of amine present.

The problem why compound IV does not react at all under the same conditions

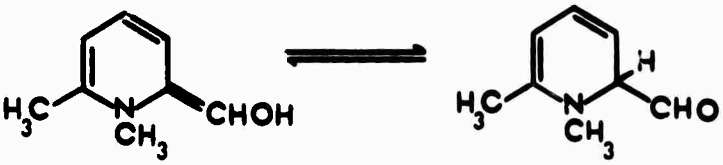


IV

used above is not understood. But one possibility might be that the 6-methyl group neighboring the quarternized nitrogen is more acidic than the methylene adjacent to the oxygen with its lone electron pairs. Or, that the possibility of the system to undergo the following mesomerism



reduces much the chance to form the ketoform of the enol



which would be subsequently attacked by a second molecule in the enolic form.

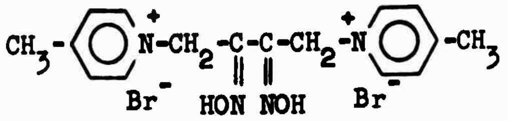
Aside from the problem of the oxidative coupling another one, namely the oxidation of the vic-glycol to the α-diketone came up. There are very few examples known where an oxidation of such a system without C-C cleavage occurs. An investigation by Littler[4] on the other hand claims that secondary and tertiary glycols are oxidized by V^{V} and Cr^{VI} salts to the corresponding diketones. Experiments on the model compound III yielded with both kinds of metal salts highly insoluble, bright yellow complexes which, under rough hydrolytic conditions (6N HCl, refl. 6^{h}), were partially destroyed. But no diketone could be isolated. This fits the observation by Slak and Waters[5], who reported that hydrobenzoin, benzpinacol and pinacol all gave insoluble complexes with chromyl chloride, which gave cleavage products in good yields on rough hydrolysis.

Facing all these difficulties, and, in addition, the fact that it seemed more and more necessary to use the corresponding quinoline derivative of I to obtain reasonably stable dye derivatives (the starting material for which would be extremely difficult to obtain) we decided to stop this pathway for a model compound and instead to investigate a similar system, described in the next section.

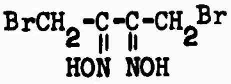
III. A modified model compound of the platinum-glyoxime type

Introduction

It has been shown in the previous section, that the quarternization of the pyridine nitrogens is not easily achieved in the picolyl-glyoxime type ligand systems (e.g. I). Therefore, we searched for ways to by pass this problem. First, we attempted to synthesize V, starting with 1,4-dibromo-2,3-butanedione (VI).



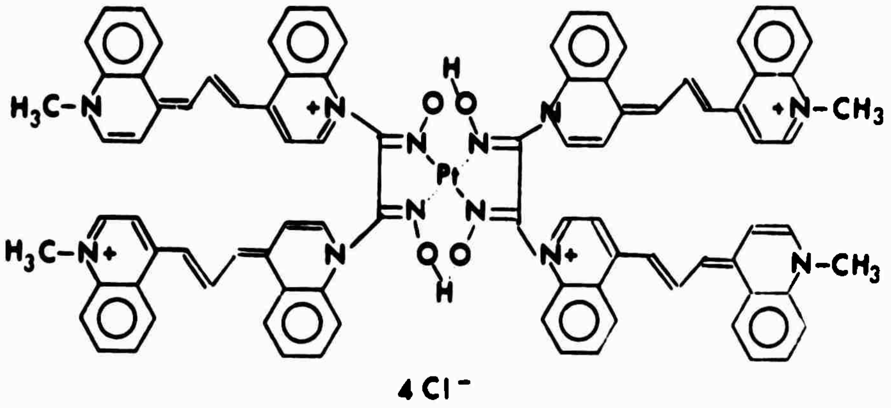
V



$BrCH_2-\underset{\underset{HON}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-CH_2Br$

VI

Experiments showed however, that this pathway is not straightforward. Instead, a synthesis of the following complex VIIa seemed more promising.

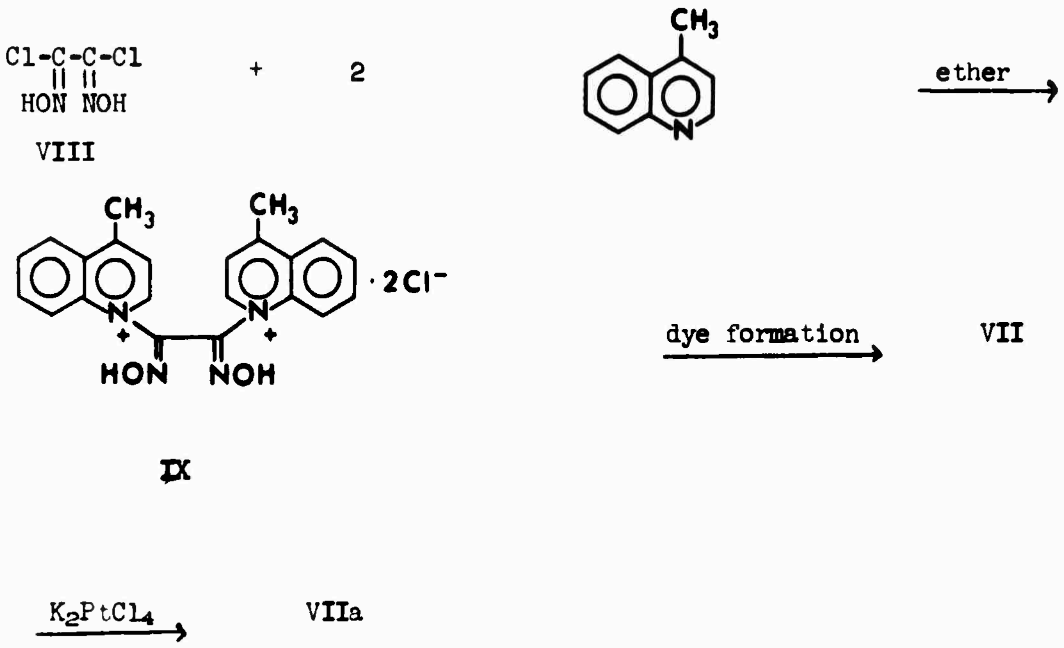


VIIa

In this compound the central Pt-atom is again surrounded by four polarizable units and the spine is formed by a Pt-Pt chain on crystallization.[2] But, in structure VII the glyoxime system itself is used to activate the aromatic methyl groups for the dye forming reaction. By this means, the mentioned difficulties of the quarternization are avoided, at the same time improving the interaction between spine and polarizable unit.

Synthesis

The synthetic work of VIIa was started in early June 1971, so that this report gives only first results. The synthetic pathway to VIIa follows:

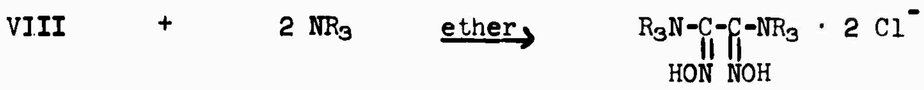


Dichloroglyoxime

Dichloroglyoxime (VIII) is commercially available (Eastman Kodak). Due to the inordinately long delivery time it has also been prepared by the following method:[6-8]

$$\text{Glyoxal} \xrightarrow{NH_2OH.HCl} \text{glyoxime} \xrightarrow{Cl_2} \text{VIII}$$

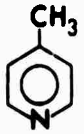
Reaction of dichloroglyoxime (VIII) with tertiary amines



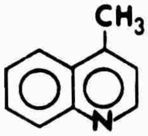
$$\mathrm{VIII} + 2\,\mathrm{NR_3} \xrightarrow{\text{ether}} \mathrm{R_3N{-}}\underset{\substack{\| \\ \mathrm{HON}}}{\mathrm{C}}{-}\underset{\substack{\| \\ \mathrm{NOH}}}{\mathrm{C}}\mathrm{{-}NR_3} \cdot 2\,\mathrm{Cl}^-$$

$\mathrm{NR_3}$:

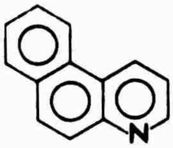
X



XI



IX

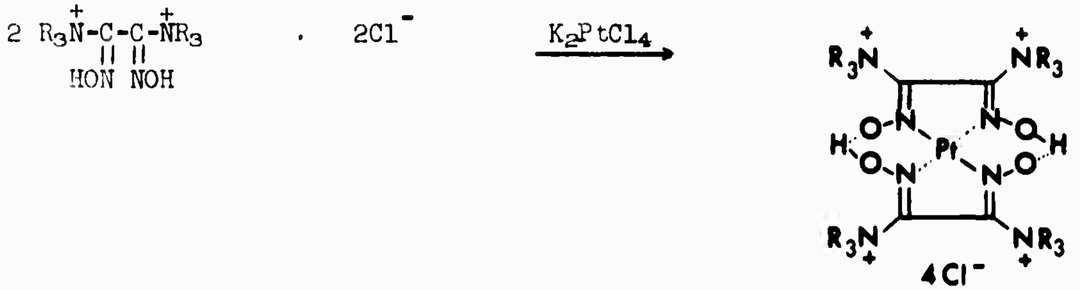


XII

The reaction products of VIII and pyridine (X), quinoline and tri-n-butylamine are already known[8,9]. We repeated the preparation of X and synthesized the adducts with 4-picoline (XI), lepidine (IX) and 5,6-benzoquinoline (XII). The reactions were carried out at room temperature in ethyl ether. Under these conditions 4-phenylpyridine gave almost exclusively the mono adduct, according to the microanalysis; whereas 7,8-benzoquinoline did not react at all. IX and XI have been prepared to carry out cyanine dye chemistry involving their activated methyl groups (see below).

XII has been made in order to obtain promptly a platinum complex with a very simple polarizable unit, the 5,6-benzoquinolinium system. This complex would allow initial conductivity measurements to be made.

Platinum complexes

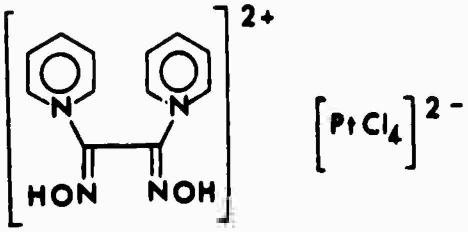


$$2\ R_3\overset{+}{N}-\underset{\underset{HON}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-\overset{+}{N}R_3 \quad \cdot \quad 2Cl^- \quad \xrightarrow{K_2PtCl_4}$$

XIII

XIIIa R_3N = **pyridine**

Reactions to form the complex have been carried out primarily with X. If the aqueous solutions of K_2PtCl_4 and X are mixed a cream colored precipitate is formed. The microanalysis shows atomic ratios which are near to those calculated for the complex. But the atomic ratios of Pt and Cl are too high, due to a side reaction which leads to XIV. IX and XI show similar behaviors. All attempts to recrystallize the product from hot water, ethanol or dimethyl sulfoxide led to the formation of a bulky brown material with a very high Pt content (over 40%). The reaction of K_2PtCl_4 with X in hot acetic acid, corresponding to that with dimethylglyoxime,[10] gave the analytically pure, crystalline compound XIV, which is most likely the following salt:



XIV

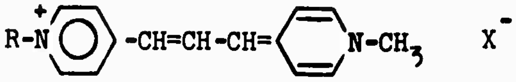
Structure XIV is strongly supported by the IR spectrum (KBr). Its fingerprint region is very similar to that of X and at the same time quite different from that of complex XIIIa (see below). ν_{Pt-Cl} appears at 325 cm^{-1} as in K_2PtCl_4 (KBr) in the form of a strong narrow band.

If X is dissolved in a water/pyridine (10:1) mixture and then reacted with an aqueous K_2PtCl_4 solution a yellow precipitate of low Pt content (17.3% Pt instead of 23.7% calc.) is formed which could not be recrystallized without decomposition. X was dissolved in an equimolecular solution of $NaHCO_3$ in water and then reacted with an aqueous K_2PtCl_4 solution. Thereby a cream colored crystalline precipitate (XIIIa) was formed, which is the dihydrate of the platinum complex of X, according to microanalysis. The IR spectrum in KBr of XIIIa resembles that of platinum dimethylglyoxime (KBr) in general character with a broad absorption going over the whole range of the spectrum (4000-250 cm^{-1}). In the fingerprint region, the strongest peaks of X emerge from that broad band. To determine whether this is due to an electronic absorption, polarized IR measurements will be required. There is no strong absorption at 325 cm^{-1}. Reactions of X with Ni(II) in aqueous solution were unsuccessful under all the above conditions. Further experiments are in progress.

The high concentration of positive charge surrounding the Pt(II) central atom makes the formation of platinum complexes of type XIII more difficult than of uncharged platinum glyoxime complexes. Therefore, the synthesis of dye substituted ligands was undertaken simultaneously. These ligands would undergo complex formation more readily, since the positive charge on the pyridine nitrogens were distributed over the long conjugated systems of the cyanine dye substituents.

Dye formation

Experiments to form glyoxime type ligands with cyanine dye substituents were carried out on IX and XI. For experimental-practical reasons we limited ourselves at this point to the formation of trimethine-cyaninedye systems, of the type XV:



XV

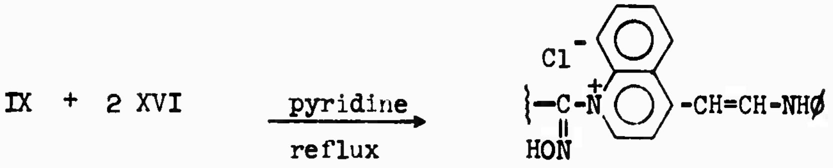
The adequate reaction with the picolinium derivative XI (described more specifically below for the lepidinium system IX) gave a dye with a typical cyanine absorption peak at 615 nm. The reported value for XV ($R=CH_3$) is 600 nm.[11] The product showed an extremely high sensitivity towards air and light and was not isolated undestroyed. This behavior is in accordance with the "normal" 4,4'-picolinium-trimethine-cyanine systems.[11] As the stability of the corresponding quinolinium derivatives is much higher, we concentrated our work on the di-lepidinium-glyoxime-dichloride (IX) as starting point.

There are a number of methods described in the literature[12] to form trimethine cyanine dyes. The two most straightforward ones use either N,N'-diphenylformamidine (XVI)

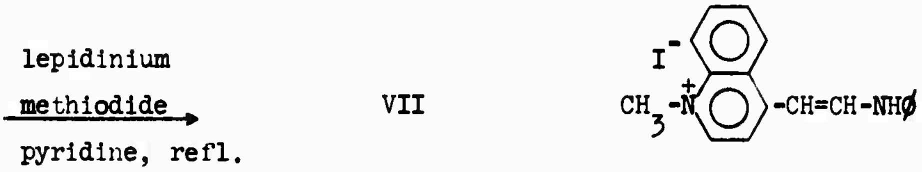
$$C_6H_5\text{-N=CH-NH-}C_6H_5$$

XVI

or a 1:1 molar mixture of aniline and an orthoformic ester, which also yields the formamidine as an intermediate. Aside from the comparatively good yields, the synthesis of asymmetric dye systems are made possible by these methods, as is required by the project. The pathway specifically for our problem is shown next:



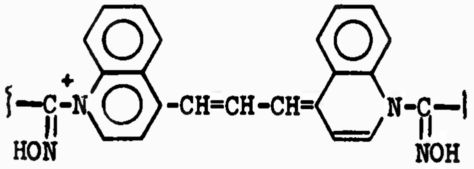
XVII
isolable intermediate



XVIII

The use of aniline/orthoester mixtures turned out to be much more efficient in respect to yield and purity of substance XVIII (see below).

Of course, it is also possible to prepare the 2-anilino-vinyl-quinolinium-methiodide (XVIII), subsequently reacting it with IX. In fact, the latter way proved to be more convenient, because we have not got the above glyoxime derivative XVII very pure so far, whereas XVIII shows an excellent analysis and sharp melting point (252°) after two recrystallizations from boiling acetonitrile. Both anilinovinyl compounds show the same absorption spectrum in the visible (λ_{max} at 480nm; broad band), indicating that also the glyoxime intermediate is in fact the one wanted. High purity of the intermediates is an absolute requirement, for the yields of the final dye forming step are pretty low (ca. 10%). We have to be sure that it is not the impurities which form the dye: i.e. if XVIII was contaminated with lepidinium-methiodide, the dye might be just ordinary N,N'-dimethyl-cryptocyanine. In reality, this problem is rather serious, because it seems as if the wanted product had its dye peak at the same position (710 nm) as the corresponding cryptocyanine itself. Furthermore its chromatographic behavior is very similar, which makes purification difficult. The microanalysis and quantitative ε-measurements both need very high purity products in order to distinguish between VII and the cryptocyanine. But there are some positive hints, that we are not dealing with an artifact: the desired product is more soluble in water and less in chloroform than the N,N'-dimethylcryptocyanine, that was also prepared. The melting point of the latter is 296°, that of the former above 300° (though, from one experiment, we got a sample with mp. 286°). But the most striking fact is that, on treatment of IX with aniline/orthoester in a trace of pyridine, we also got a cyanine dye with its peak at 710 nm, presumably of the type XIX:

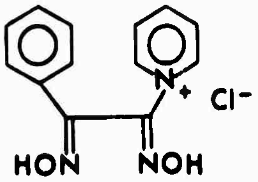


XIX

By this experiment we excluded the possibility of dye formation due to impurities, as IX has never seen a lepidinium salt other than itself.

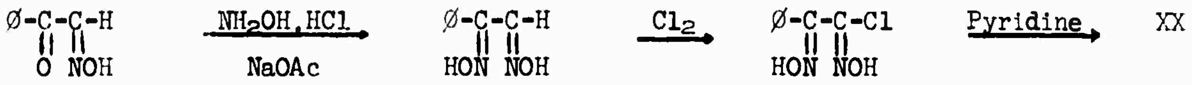
1-phenyl-2-pyridinium glyoxime chloride

The highly concentrated positive charge surrounding the central platinum atom, which makes the complex formation difficult, can also be reduced by exchanging one tertiary amino group against a phenyl group, sacrificing two



XX

polarizable units per platinum atom in the complex. XX was synthesized according to the following scheme:



$$\underset{\text{O}\ \ \text{NOH}}{\emptyset\text{-}\overset{}{\text{C}}\text{-}\text{C-H}} \xrightarrow[\text{NaOAc}]{\text{NH}_2\text{OH.HCl}} \underset{\text{HON}\ \ \text{NOH}}{\emptyset\text{-C-C-H}} \xrightarrow{\text{Cl}_2} \underset{\text{HON}\ \ \text{NOH}}{\emptyset\text{-C-C-Cl}} \xrightarrow{\text{Pyridine}} \text{XX}$$

The first 2 steps have already been described.[13,14] The last step, the salt formation, was carried out in dry ethyl ether at room temperature in the dark. Complex formation reactions are in progress.

IV. Experimental section

General Remarks

This section gives only the data for completed results. Experiments still in progress are not listed. Procedures already reported in the literature are not described, even if minor modifications were applied. All melting points are uncorrected. The NMR spectra were measured on a Varian T-60 (MHz) spectrometer (TMS internal = 0.0 ppm, S singlet, D doublet, M multiplet).

Dipyridinium glyoxime dichloride (X)

Prepared according to A. Quilico:[9] $C_{12}H_{12}N_4O_2Cl_2$ (315.16)

Calc. %	C	45.73	H	3.84	N	17.78	O	10.15	Cl	22.50
Found		45.65		3.87		17.90				22.74

The mass spectrum shows no molecular peak, but primarily the cleavage pattern of pyridine and dicyano-di-N-oxide.

MS: m/e 152 (1.4%), 145 (1.4), 144 (3.5), 136 (4.2), 135 (2.1), 120 (26), 104 (8), [illegible] (29), 84 (29), 80 (29), 79 (88), 78 (46), 68 (47), 54 (20), 53 (4), 52 ([illegible]), 51 (60), 50 (56), 49 (20), 45 (17), 44 (100), 43 (80), 42 (60), 41 (26), 39 (54).

Dilepidinium glyoxime dichloride (IX)

1.5[illegible] g VIII were dissolved in 100 ml dry ether. 10 ml lepidine in 10 ml dry ether were immediately added. The reaction mixture was allowed to stand for 1/2 hour at room temperature in the dark. On mixing of the components, a precipitate started to form. The ether solution which had turned yellowish was decanted off. The colorless precipitate was washed three times with 20 ml ether and then dissolved in as few as possible 2 N HCl. The mixture was evaporated to dryness at reduced pressure. The residue was recrystallized from methanol/ether, forming bright colorless needles (mp 149-151°C, after two recrystallizations). Yield 2.45 g (55%). A further, less pure crop can be obtained from the decanted mother liquor of the reaction after standing at room temperature for 3 days. Dihydrochloride (cf. ref. 9, pg. 210) of IX: $C_{22}H_{22}N_4O_2Cl_4$ (516.25)

Calc. %	C	51.18	H	4.30	N	10.85	O	6.20	Cl	27.47
Found		52.95		4.62		10.14				25.68

NMR (D_2O, <u>H</u>DO = 4.80 ppm): 2.93 (S: methyl groups, 6H), 8.04 (M: H_3, H_5, H_6, H[illegible], H_8, 10 H), 8.90 (D: H_2, 2H)

Di-4-picolinium glyoxime dichloride (XI)

XI was obtained following the procedure described for IX with the same yield. Recrystallization from methanol/ether gave colorless rhombic crystals.

XI decomposes slowly above 160°C and melts finally between 234 and 235°C dec. $C_{14}H_{16}N_4O_2Cl_2$ (343.21)

Calc. %	C	48.99	H	4.69	N	16.32	O	9.32	Cl	20.66
Found		48.7		4.6		16.6				20.6

NMR (D_2O, HDO = 4.80 ppm): 2.90 (S: methyl groups, 6H), 8.24 (M: H_3, H_4, 4H). 9.00 (M: H_2, H_6, 4H)

Di-5,6-benzoquinolinium glyoxime dichloride (XII)

The preparation of XII is similar to that of IX. 0.80 g VIII in 50 ml dry ether were mixed with 4.15 g 5,6-benzoquinoline (Aldrich) in 50 ml dry ether. After 5 hours, a colorless precipitate was filtered off, washed 4 times with 20 ml ether and recrystallized repeatedly from 50% aqueous methanol under addition of HCl. Colorless needles (mp 227-228°C dec.), yield 1.60 g (53%). A further, less pure crop can be obtained from the mother liquor of the reaction. $C_{28}H_{22}N_4O_2Cl_4$ (588.32) dihydrochloride of XII.

Calc. %	C	57.16	H	3.77	N	9.52	O	5.44	Cl	24.10
Found		57.07		3.86		9.61				23.80

Bis(dipyridinium glyoximato) platinum (II) tetrachloride dihydrate (XIIIa)

63 mg X were dissolved in a solution of 18 mg $NaHCO_3$ in 50 ml water and then 42 mg K_2PtCl_4 in 2 ml water were added. The cream colored crystals formed during 3 hours were filtered off and washed thoroughly with water and ether. Yield 65 mg (75%). The compound starts to turn dark above 220°C and does not melt up to 330°C. $C_{24}H_{26}N_8O_6Cl_4Pt$ (859.42)

Calc. %	C	33.54	H	3.05	N	13.04	O	11.17	Cl	16.50	Pt	22.70
Found		33.43		2.79		13.08				16.53		22.22

Salt of X with $PtCl_4^{2-}$ (XIV)

51[illegible] mg X and 20[illegible] mg K_2PtCl_4, both dissolved in 50 ml hot $HOAc/H_2O$ 1:1 mixture, were mixed. On cooling, brown crystals were formed, filtered off and washed twice with cold HOAc and twice with ethyl acetate. Branched needles (mp 2[illegible]-300°C dec.), yield 80 mg. $C_{12}H_{12}N_4O_2Cl_4Pt$ (584.16)

Calc. %	C	24.67	H	2.07	N	9.59	O	5.48	Cl	24.79	Pt	33.40
Found		24.67		2.03		9.83				24.53		33.48

1-Phenyl-2-pyridinium glyoxime chloride (XX)

Phenylglyoxaldoxime (Baker) was converted into phenylglyoxime[13] and this in turn into phenylchloroglyoxime[14]. 0.40 g phenyl-chloro glyoxime dissolved in 200 ml dry ether were mixed with 20 ml dry pyridine at room temperature and allowed to stand in the dark for 4 days. The colorless precipitate formed was filtered off from the pink mother liquor. Yield 0.51 g (91%). Recrystallization from 60% ethanol under addition of HCl gave colorless crystals (mp 201-202°C dec.). $C_{13}H_{12}N_3O_2Cl$ (277.71)

Calc. %	C	56.22	H	4.36	N	15.13	O	11.52	Cl	12.77
Found		56.12		4.36		15.06				12.53

NMR (DMSO-d_6): 3.40 (S: H_2O of the solvent and part of the oxime-OH, 2.5 H), 7.43 (M: phenylprotons, 5H), 8.33 (M: H_3,H_5 in pyridine nucl., 2H), 8.90 (M: H_4 in pyridine nucl., 1H), 9.33 (M: H_2,H_6 in pyridine nucl., 2H), 12.38 (S: part of oxime-OH, 0.5H)

V. Related Experiments

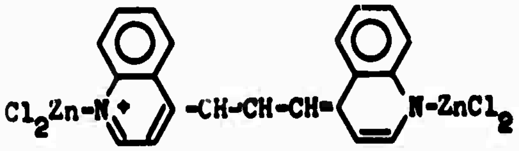
Model Compounds for an excitonic insulator

In connection with the excitonic insulator,[15] alkyl substituted platinum glyoxime complexes were prepared as model compounds. Bis-(dimethylglyoximato)-platinum II was prepared according to the literature (cf. ref. 16 and others). Recrystallization from boiling nitrobenzene gave dark red shiny needles. (Pt-Pt distance 3.26 ± 0.02 A) Bis(nioximato)-platinum II was prepared by the same method: dark brown needles, (Pt-Pt distance 3.26 ± 0.02 A).

Bis(di-undecylglyoximato)-platinum II (XXI) was prepared by the following procedure: 220 mg K_2PtCl_4 were dissolved in 10 ml water and 418 mg di-undecylglyoxime[17] in 35 ml THF were added. During 4 days a total of 55 mg Na_2CO_3 was added to maintain approximate neutrality. Thereafter, the reaction mixture was evaporated and the dark residue was chromatographed on silica gel Merck PF_{254} (benzene/chloroform 7:1). The chromatography was repeated twice yielding 327 mg of XXI. ($R_f = 0.43$) Recrystallization from benzene/EtOH gave small orange needles (mp. 72-73°). In solution XXI a red side product ($R_f = 0.37$) formed slowly, which can be removed by chromatography. The mass spectrum shows the molecular peak at m/e 985, a typical hydrocarbon cleavage pattern and an α-cleavage $M-C_{11}H_{23}$ (m/e 830) proved by a metastable peak at m/e 700 (calc. $985 \longrightarrow 830$: 699.4). Attempts to measure the Pt-Pt distance by a powder diffraction pattern were not conclusive. Therefore, crystal growing experiments are in progress.

A Zinc-Cyanine-Dye

It would be of some advantage to bring the dye system even nearer to the spine than in VII. One possibility could be to coordinatively bind the metal of the spine to one end of the dye, as shown in formula XXII:



XXII

There still would be no direct conjugation between spine and polarizable unit (the orbitals standing perpendicular to each other), but the interaction would be as strong as possible.

It is known from the chemistry of the pyridines, that anhydrous $ZnCl_2$ activates 2- and 4-methyl groups just the same as quarternization does.[19] So, instead of starting with lepidinium methiodide, one could expect the lepidine-$ZnCl_2$ complex to undergo the dye formation, which is indeed the case, as preliminary experiments have shown. (Cyanine type absorption at 710 nm; lepidine and excess anhydrous $ZnCl_2$ were refluxed for 10 minutes with aniline/orthoester.) The dye, as expected, is immediately destroyed upon addition of water. Unfortunately, we were unsuccessful so far to carry out the same reaction with d^8 transition metals.

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RESEARCH REPORT

Joseph San Filippo

May, 1971

Summary: The results of several synthetic approaches to the preparation of polymeric chains of metal atoms are discussed.

Introduction and Discussion: Two classes of substances are recognized to possess the semi-conductive spine necessary to test the exciton theory of superconductivity. The first class consists of transition-metal atoms interacting in the crystalline state, along the principal axis of the single crystals. This class is not readily modified through chemical synthesis and will not be discussed further.

The second class consists of molecules containing polymeric chains of metal atoms held together by truly covalent bonds. The properties of these "molecular metals" are subject to modification by chemical synthesis and can, therefore, provide a direct means of comparing theory and experiment. In view of the semi-conductive properties of single crystals having chains of metal atoms, it is felt that in a condensed state molecules possessing a spine of covalent metal bonds will exhibit an anisotropic conductivity. It is further felt, although the problem of charge carriers passing between such one-dimensional molecules remains unresolved, that a chain length of 30 - 50 metal atoms may be required before the intramolecular properties dominate the intermolecular properties in these systems. Thus, the investigation of synthetic procedures which would yield specific molecular sizes, rather than a random range of molecular weights, was undertaken with initial investigations centering around Group IV elements because of their demonstrated capacity to catenate through covalent bonds.

Organogermanium compounds have several properties which suggested that germanium oligomers could be successfully employed as monomers in this study. First they are air-stable and sufficiently volitile that they can be distilled or subjected to glpc and mass spectrographic analysis. Second, energetic considerations suggest a modest band gap for germanium chains and higher energy conduction electrons could be introduced by incorporating Se, Te, or a transition-metal atom into the chain. The major disadvantage of germanium is that there is no reaction at present which permits the selective coupling of two germanium atoms as required for the preparation of germanium oligomers. For this reason, an investigation of potential germanium-germanium bond forming reactions was undertaken.

Hydrostanolysis provides an efficient, selective means of forming tin-tin bonds.

$$R_3Sn-H + R'_3Sn-NR''_2 \longrightarrow R_3Sn-Sn-R'_3 + R'_2NH$$

This procedure is largely unsuccessful when adopted to the preparation of germanium-germanium bonds. In view of

$$R_3GeH + R'_3GeNR''_2 \not\longrightarrow Re_3Ge-GeR'_3 + R''_2NH$$

the mechanism suggested for hydrostannolysis[1], it was felt that increasing the electron density at the nitrogen center might affect the desired reaction.

Based on a simple valence bond view, the aside group can be expected to place significant electron density on the inner most nitrogen. Therefore, $R - N = \overset{+}{N} = \overset{-}{N} \longleftrightarrow R - \overset{-}{N} - \overset{+}{N} \equiv N$

at attempt was made to couple an alkylgermanium aside with an organogermane. When performed under a variety of conditions, this reaction failed to produce the desired product and returned only starting materials.

$$Et_3GeN_3 + Ph_3GeH \underset{\Delta}{\not\longrightarrow} Et_3Ge\text{-}GePh_3 + HN_3\uparrow$$

Chains containing no more than two germanium atoms are readily preparable by the reaction of an organogermanium halide with a lithium organogermane. However, $R_3GeLi + R'_3GeX \longrightarrow R_3Ge - GeR'_3 + LiX$ the utility of this procedure is decreased as the length of the chain is increased, due to the accompanying facile cleavage of germanium-germanium bonds which also occurs under these conditions. In an effort to overcome this latter reaction, a system employing a more covalent germanium-metal reagent was examined.

Bis[triphenylgermanium](bipyridyl)zinc(II) (1) is a stable, relatively oxygen insensitive compound.[1] These properties recommend this reagent as a potentially useful one for the synthesis of germanium-

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[1] H. M. J. C. Creemers, Ph.D. Thesis, Utrecht University, 1969.

germanium bonds by reaction with an appropriate substrate such as, for example, an organogermanium halide. This contention was supported by the fact that **1** reacted readily with methyl iodide to produce methyltriphenylgermane. Accordingly, the reaction of **1** with triethylgermanium chloride was investigated. However, under a variety of conditions, this reaction failed to yield any of the desired unsymmetrical digermane coupling product. Analysis of the reaction

$$[Ph_3Ge]_2\,Zn \cdot (bipy) + 2\,Et_3GeCl \not\longrightarrow 2\,Ph_3Ge-GeEt_3 + (bipy)\cdot ZnCl_2$$

showed only unreacted starting materials.

The formation of tin-tin bond by the overall reaction represented below, is well documented[1] Organogermanes do not undergo a similar

$$2\,R_3SnH \xrightarrow[\text{(eg}\,Et_2NH)]{\text{catalyst}} R_3Sn-SnR_3 + H_2\uparrow \qquad (1)$$

dehydrogenative coupling, presumably because the germanium-hydrogen bond is considerably stronger than the tin-hydrogen bond. However, germanium hydrides which are also substituted with one or more transition metal centers, have been noted to display a reactivity similar to that of the more reactive organotin hydrides. Thus, for example, bis[cyclopentadienyl(dicarbonyl)iron] germanium dihydride reacts rapidly with chloroform at room temperature.[2]

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[2] N. Flitcoft, D. A. Harbourne, I. Paul, P. M. Tucker and F. G. A. Stone, J. Chem. Soc. A, 1130 (1966).

$$[Cp(CO)_2Fe]_2\,Ge\,H_2 \xrightarrow{CHCl_3} [Cp(CO)_2Fe]GeCl_2$$

The marked similarity in reactivity between bis[cyclopentadienyl-(dicarbonyl)iron] germanium dihydride and tin hydride in this respect suggested that such an intermediate might provide a convenient route to transition-metal substituted germanium oligomer by a hydrogen extrusion process similar to that observed for tin (eq. 1). When this reaction

$$m\,[Cp(CO)_2Fe]_2GeH_2 \xrightarrow[-mH_2]{catalyst} \left([Cp(CO)_2Fe]_2Ge\right)_m$$

was carried out in refluxing benzene using diethylamine as a catalyst, only unreacted hydride was recovered.

An attractive approach to the preparation of linear intermetallic chains is suggested by a monomer unit containing a specific ratio of transition-metal and tin or germanium atoms. A planar tetradentate ligand about the transition metal center would prevent cyclization or clustering of the metal atoms. Polymerization could be accomplished presumably by taking advantage of the amine catalyzed coupling of tin hydrides discussed above. This approach has been attempted with some success in these laboratories, utilizing difunctional compound 2.

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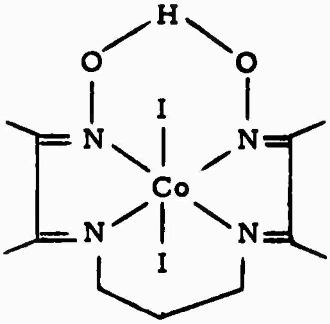
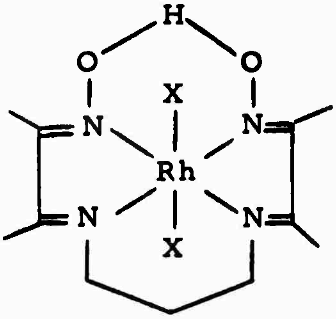
[3] Private communication from D. Murphy.



2

In view of the fact that metal-metal bonds involving a second or third row transition metal appear to be significantly stronger than the analogous system employing a first row transition metal, it was felt that the desirable properties of the cobalt system (2) could be incorporated into and enhanced by employing the analogous rhodium system (3). Unfortunately, such systems are unknown, hence a synthesis of this compound was undertaken.



X = Cl, Br, I

3

The substitution inertness of the rhodium(III), combined with the fact that the substitution labile +2 state is quite uncommon for rhodium, prevent the ready preparation of most rhodium(III) complexes by procedures which have proven successful for synthesis of the analogous cobalt compounds. For this reason virtually all the preparations of the few quadridentate Schiff base complexes of rhodium(III) reported to date have involved the presence of a suitable reducing agent such as ethanol,[4] sodium borohydride,[4] hydroazine,[4] hypophosphorus acid,[4] or zinc amalgam;[4,5] for example,

$$RhCl_3 \cdot XH_2O + 2(dmgH) \xrightarrow[80°]{EtOH/py} py \cdot Rh(dmg)_2Cl$$

dmgH ≡ N, N'-dimethylglyoxime

The most recently reported preparation of a quadridentate Schiff-base complex of rhodium(III) is that of chloro(salen)(pyridinato)rhodium(III) (4) produced by the action of zinc dust on rhodium trichloride (hydrate) in a hot methanolic pyridine solution of N, N'-ethylenebissalcylideneiminato, abbreviated as salen.[5]

$$RhCl_3 \cdot XH_2O + \text{salen} \xrightarrow[\substack{MeOH/py \\ 80°}]{Zn} \underset{4}{py \cdot Rh(salen)Cl}$$

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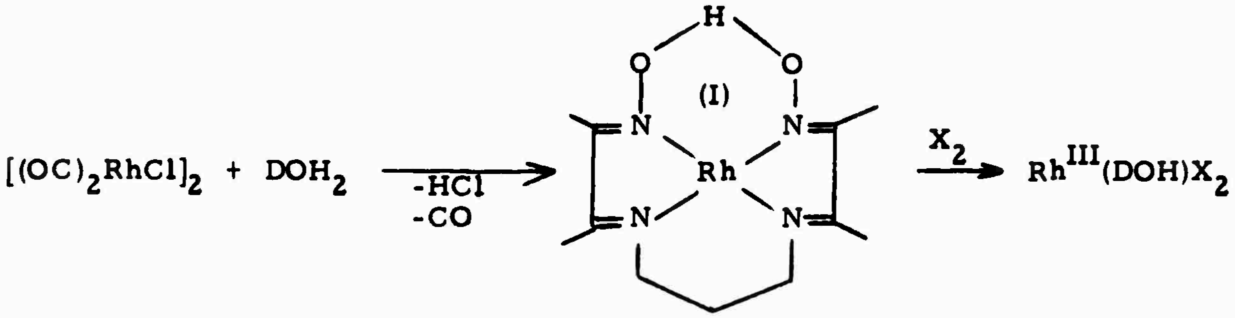
[4] R. D. Gillard, J. A. Osborn, and G. Wilkinson, J. Chem. Soc. 1951 (1965).

[5] R. J. Cozens, K. S. Murray, and B. O. West, Chem. Comm. 1262 (1970).

Following the successful repetition of the above reaction, an attempt was made to adopt this procedure to the preparation of 3. A number of attempts were carried out under slightly different conditions, but in each instance the product proved to be an intractable brown solid which exhibited a very broad, ill-defined infrared spectrum. Similar results were obtained when zinc amalgam and sodium borohydride were employed as reducing agents.

The lability of rhodium(I) to ligand substitution suggested that perhaps 3 could be obtained by oxidation of the corresponding tetracoordinate complex of rhodium(I) with the desired univalent Schiff-base ligand, (eg. 5.)



5

Such complexes of rhodium are unknown and several attempts to prepare 5 by reaction of DOH_2 with μ-chloro(dicarbonyl)rhodium(I) were unsuccessful,[6] producing only uncharacterizable solids.

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[6] Bridge splitting reactions of $[Rh(CO)_2Cl]_2$ with amines have been reported by Wilkinson as also yielding uncharacterizable solids: D. N. Lawson and G. Wilkinson, J. Chem. Soc. 1900 (1965).

Wilkinson has reported that certain ligand substitution reactions can be carried out directly on rhodium(III) species under special conditions.[4] Under these conditions, dichloro(tetrapyridinato)rhodium(III) salts, when refluxed in aqueous solutions containing an excess of a relatively non-volatile second ligand, pyridine is dispelled from the rhodium complex. By removing the pyridine as it is formed, the reaction is driven to completion.

$$[(py)_4RhCl_2]^+ + 4L \xrightarrow[\Delta]{} [L_4RhCl_2]^+ + 4py\uparrow$$

This procedure suggested that a similar technique might allow the preparation of 3. However, although the evolution of pyridine was noted in every instance, numerous attempts to prepare 3 in this manner produced only hydrolyzed ligand and various aquo rhodium(III) salts.

$$[(py)_4RhCl_2]^+ + DOH_2 \not\xrightarrow[\Delta]{} \underset{3}{Rh(DOH)Cl_2}$$

Many of the desired properties which a complex such as 3 would presumably provide in syntheses directed toward the preparation of metal-metal oligomers, are potentially available with compounds which contain two metal atoms joined by strong homonuclear metal-metal bonds.[7]

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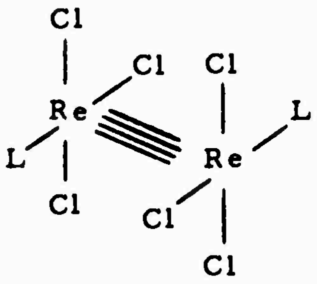
[7] F. A. Cotton, *Accounts Chem. Research*, 2, 240 (1969). and references therein.

Figure 1 shows the structures of several such compounds. These compounds and their various related derivatives have been postulated as having quadrupole metal-metal bonds.[7]



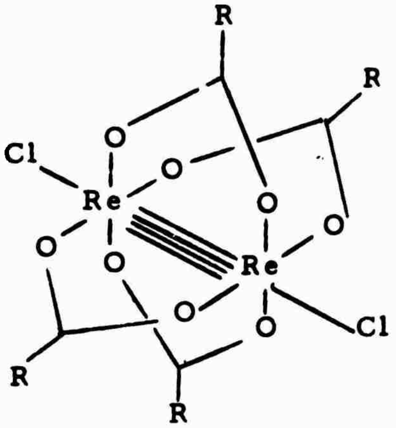
6

a, L = Et_3P

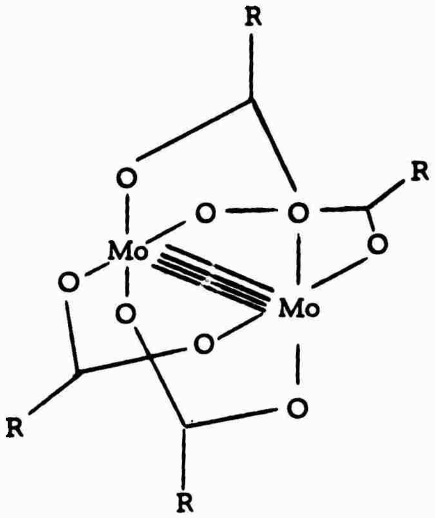
b, L = Ph_3P

c, L = Bu_3P

d, L = Cl



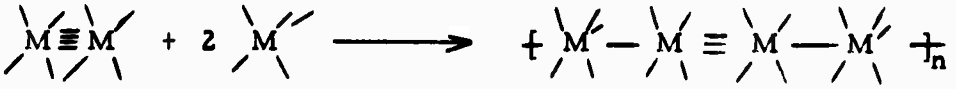
7, R = CH_3



8, R = CH_3

Figure 1.

This proposal suggested the possibility that such compounds might serve as useful monomers in reactions leading to metal-metal chains by pathways analogous to the fashion in which olefins and acetylenes are employed as monomers in organic polymerizations. For example,



(M' = d^8 metal complex)

To examine this possibility, the reaction of hexachloro-bis(tri-n-butylphosphine)dirhenate(III) (6c) with several d^8 metal complexes, including chlorocarbonylbis(triphenylphosphine)iridium(I) and μ-chloro(dicarbonyl)rhodium(I), were investigated. Invariably, these reactions afforded only unreacted starting materials. Indeed, the analogy of multiple metal-metal bonds to carbon π-systems would seem, on the basis of a cursory investigation of chemical reactivity, to be unwarranted.[8]

Tetracarboxylatodichlorodirhenate(III) (7) represents a potential alternative to the quest for bifunctional functional monomer similar to 3, provided the terminal halides can be replaced by a metal or metalloid

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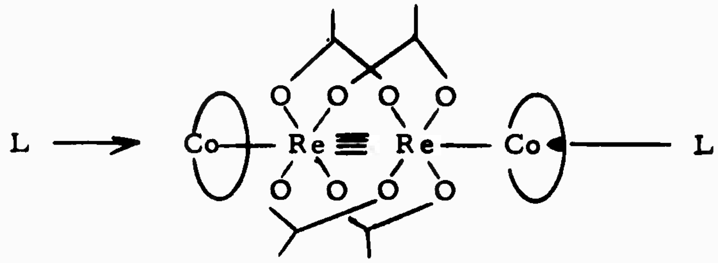
[8] It was observed, for example, that unlike olefins and acetylenes, multiple metal-metal bonds do not react with bromine, even after several hours at room temperature.

center, thereby enabling the preparation of a linear metal-metal system. For example, a related reaction was envisioned as producing a linear

$$Re_2(OAc)_4Cl_2 + 2\ L \cdot (dmg)_2\ Co^{(I)} \longrightarrow$$

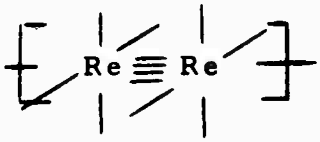
7



chain of atoms by the following scheme.

$$Re_2(OAc)_4Cl_2 + NaBH_4 \longrightarrow Re_2(OAc)_4H_2$$

$$Re_2(OAc)_4H_2 \xrightarrow{-H_2}$$



When carried out, each of the reactions outlined above produced only unreacted starting dirhenate. The substitution of diisobutylaluminum hydride for sodium borohydride produced a reaction, the only isolable product from which was a small amount of a gelatanous brown substance. This material displayed an uncharacterizable ir spectrum and was insoluble in all solvents.

During the course of the investigation of the dirhenate(III) complexes outlined above, it became desirable to have derivatives which would be readily soluble in organic solvents. The two known complexes, hexachlorobis(triphenylphosphine)dirhenate(III)(**6a**) and -bis(triethylphosphine)-dirhenate(III), (**6b**) are either slightly soluble, as in the latter instance, or completely insoluble, as in the former case. Accordingly, the tri-*n*-butylphosphine analogue was prepared. As anticipated, **6c** is

$$[Bu_4N]_2Re_2Cl_8 + 2\,Bu_3P \xrightarrow[25°]{MeOH} \underset{\textbf{6c}}{Re_2Cl_6(n\text{-}Bu_3P)_2}$$

nicely soluble in a broad spectrum of organic solvents.

The considerable difference in solubilities of the triphenylphosphine and tri-*n*-butylphosphine complexes suggested that it would be relatively easy to isolate the unsymmetrically substituted complex hexachloro(triphenylphosphine)(tri-*n*-butylphosphine)dirhenate(III) (**10**). Such a complex would be desirable for investigations aimed at examining possible rotational isomerism about the rhenium-rhenium bond in dirhenate(III) systems, as determined by nmr techniques. Indeed, it was found that **10** could be readily obtained and in good yield, by making use of the considerable difference in solubility of the three complexes.

$$[NBu_4][Re_2Cl_8] + n\text{-}Bu_3P + Re_2Cl_6(Bu_3P)(Ph_3P) + Re_2Cl_6(Bu_3P)_2$$

$$\underset{\text{insoluble}}{\textbf{6b}} \qquad \underset{\text{intermediate solubility}}{\textbf{10}} \qquad \underset{\text{very soluble}}{\textbf{6c}}$$

Cotton has described the preparation and X-ray crystallographic analysis of pentammonium(nonachloro)dimolybdenate(II) (11).[9]

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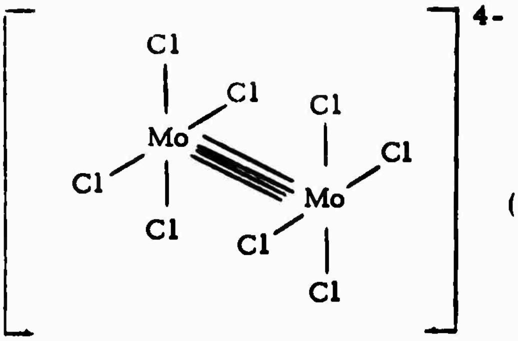
[9] F. A. Cotton and J. V. Brenic, Inorg. Chem., **9**, 346 (1970).



$(NH_4^+)_4\ (NH_4Cl)$

11

The fact that this substance is isostructural and isoelectronic with octachlorobis(tetra-*n*-butylammonium)dirhenate(II), the precursor employed in the preparation of all the dirhenate(III) complexes discussed above, suggested that 11 might serve as a similar precursor to related dimolybdenate(II) complexes. Such derivatives, if available, could provide an inexpensive substitute to the more expensive rhenium analogues under investigation. To determine the feasibility of such a proposal the synthesis of several potentially useful derivatives of this system were undertaken.

The addition of tri-*n*-butylphosphine to a methanolic suspension of 11 results in an immediate reaction, as evidenced by the rapid color change. The deep blue crystalline solid isolated by filtration, analyzed as tetrachlorotetra(tri-*n*-butylphosphine)dimolybdenate(II) (12a)

$$(NH_4)_5Mo_2Cl_9 + 4\ \underline{n}\text{-}Bu_3P \xrightarrow[0°]{MeOH} Mo_2Cl_4(\underline{n}\text{-}Bu_3P)_4$$

11 12a

Molecular weight determinations in chloroform and spectral data (*vide infra*) are consistent with this assignment. Similar reactions employing various related ligands produces analogous complexes.

$$(NH_4)_5Mo_2Cl_9 + 4L \xrightarrow[0^\circ]{MeOH} Mo_2Cl_4L_4$$

$$\begin{array}{lccc} L = & Ph_3P, & Et_3P, & (MeO)_3P \\ & \textbf{12b} & \textbf{12c} & \textbf{12d} \end{array}$$

In contrast to the dirhenate(III) system, the reactions of the dimolybdenate(II) complex 11 with phosphites provides stable, howbeit air-sensitive, phosphine complexes. This oxygen-sensitivity extends to other derivatives. Thus, unlike their dirhenate analogs, the triphenyl- and trialkylphosphine complexes 12a - c show varying degrees sensitivity to oxygen ranging from the moderately reactive complex 12b and 12d to relatively unreactive complexes 12a and 12c.

In the course of characterizing the previously unknown derivatives of hexachlorodirhenate(III) and tetrachlorodimolybdenate(II) described above, the nmr spectrum of these complexes was examined. Unlike the nmr spectrum of many phosphine metal complexes which are little changed from that of the free ligand itself, the 'H nmr spectrum of these complexes displayed marked differences from that of the free ligand. Thus, an examination of hexachlorobis(triethylphosphine)-dirhenate(III) (6a) revealed two distinct multiplets, one centered at 1.18δ, the other at 2.42δ, in a ratio of 2 : 1. By contrast the 'H nmr of free triethylphosphine consists of one complex multiplet ranging from 0.86 - 1.52δ.

Likewise, hexachlorobis(tri-*n*-butylphosphine)dirhenate (**6c**) exhibited three distinct resonances: 0.92δ (triplet, (3H), 1.36δ (br, 4H) and 2.36δ (br, 2H), while the spectrum of free tri-*n*-butylphosphine consists of one resonance at 0.95δ (triplet, 3H) and another at 1.35δ (multiplet, 6H).

The following additional observations were made. First, the addition of free ligand has no effect on the spectrum of these complexes. Second, the spectra described above remained unchanged over a temperature range of +35° to +180°. These further observations exclude, respectively, a ligand exchange process proceeding via a dissociative pathway and second-order paramagnetism[10] as being responsible for the unusual spectra of these compounds.

These and similar spectral observations on related dimolybdenate(II) complexes (*vide infra*) can be most simply explained as arising from the diamagnetic anisotropic shielding of the protons on the carbon adjacent to phosphorous, resulting from the presence of a multiple metal-metal bond.

McConnell[11] has derived an approximate relationship describing the effect of diamagnetic anisotropy caused by an axially symmetrical

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[10] For a discussion of the effects of temperature on the second-order paramagnetism and the 'H nmr spectra of several phosphine complexed rhenium(III) compounds, see: E. W. Randall and D. Shaw, *J. Chem. Soc. A*, 2867 (1969).

group of electrons, G, in which r is the distance between the proton and

$$\sigma(G) = \frac{(3\cos^2\theta - 1)(X_c - X_T)}{3r^3} \qquad (2)$$

the electrical center of gravity of G (in the present case, the mid-point of the metal-metal bond), θ is the acute angle which r makes with the symmetry axis and X_L and X_T are, respectively, the longitudal and transverse magnetic susceptibilities of the molecule in question.

It is seen that this function changes sign at θ = 55° 44'. There are, therefore, two conical regions extending from each end of a multiple bond within which the shielding σ, which affects the proton, will be positive (ie. an upfield shift results) while a proton in the region without the cone will suffer a negative or deshielding influence (ie. a down-field shift). It is important to note that the regions denoted in Figure 2 show only the

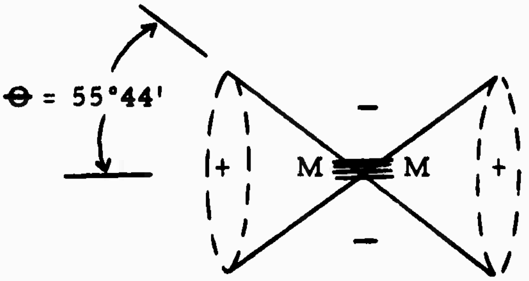

Figure 2.

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[11] H. M. McConnell, J. Chem. Phys., **27**, 226 (1957).

sign of the shielding as a function of θ. The magnitude of the shielding in each region increases towards the symmetry axis of the region and toward the electrical center of gravity of the metal-metal bond.

In general, the values of X_L and X_T for any group G can seldom be measured. In the absence of such information the quantity $(X_L - X_T)$ may be either positive or negative. For the present system, a consideration of simple geometric factors reveals that this value must be positive, ie. $(X_L - X_T) > 0$. Thus, Figure 3 illustrates the Re-Re-P bond geometry for hexachlorobis(triethylphosphine)dirhenate(III) as reported by Cotton and Foxman.[7] Knowing the Re-Re bond length (2.222 Å) and the Re-P bond distance (2.449Å) leads to a value for θ, the acute angle between the electrical center of gravity and the phosphorous nucleus, of 65° 35'. This value exceeds by a significant amount

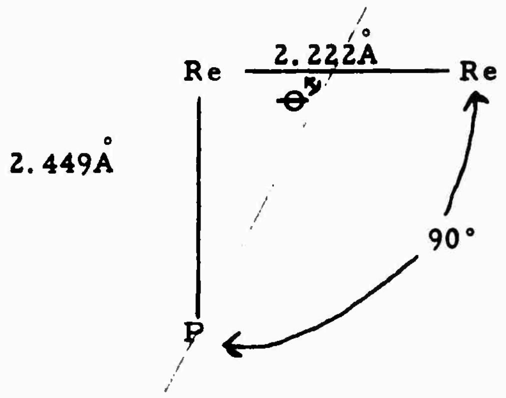


Figure 3.

the value of 55° 44' at which the function described in eq. 2 changes sign. It follows, therefore, that the proton nuclei, which of course lie below the phosphorus center and hence at an even greater angle on the average the phosphorus, must lie well without the positive cone and in the negative region pictured in Figure 2.

It is clear from the observed ^{1}H nmr spectrum that the protons on the carbon adjacent to phosphorus in hexachlorobis(triethylphosphine)dirhenate(III) and in related complexes, experience a considerable deshielding (ie. $\sigma(G) < 0$). This observation taken together with eq. 2 requires, therefore, that $(X_T - X_L) > 0$.

The strong deshielding ($\sim$1 ppm) observed in dirhenate(III) systems is also found in appropriate derivatives of the dimolybdenate(II) system, although of a somewhat lessened magnitude. Thus, for example, the ^{1}H nmr spectrum of tetrachlorotetra(tri-*n*-butylphosphine)dimolybdenate(II) (**12a**) revealed three resonances: 0.83δ (triplet, 3H), 1.32δ (multiplet, 4H) and 2.10δ (br, 2H).

A further indication that the deshielding which is observed in these systems is, in fact, the result of diamagnetic anisotropy is evidenced by the fact that it is not limited solely to protons on the centers immediately adjacent to phosphorus. A case in example is tetrachlorotetra(trimethylphosphite)dimolybdenate(II) (**12d**), the ^{1}H nmr methyl resonance for which occurs at 3.74δ ; by comparison, the same resonance in the free ligand appears at 3.52δ . Thus, as expected, in accordance with the r^{-3} dependence described by eq. 2, the magnitude of the deshielding experienced by these more remote nuclei is noticeably reduced.

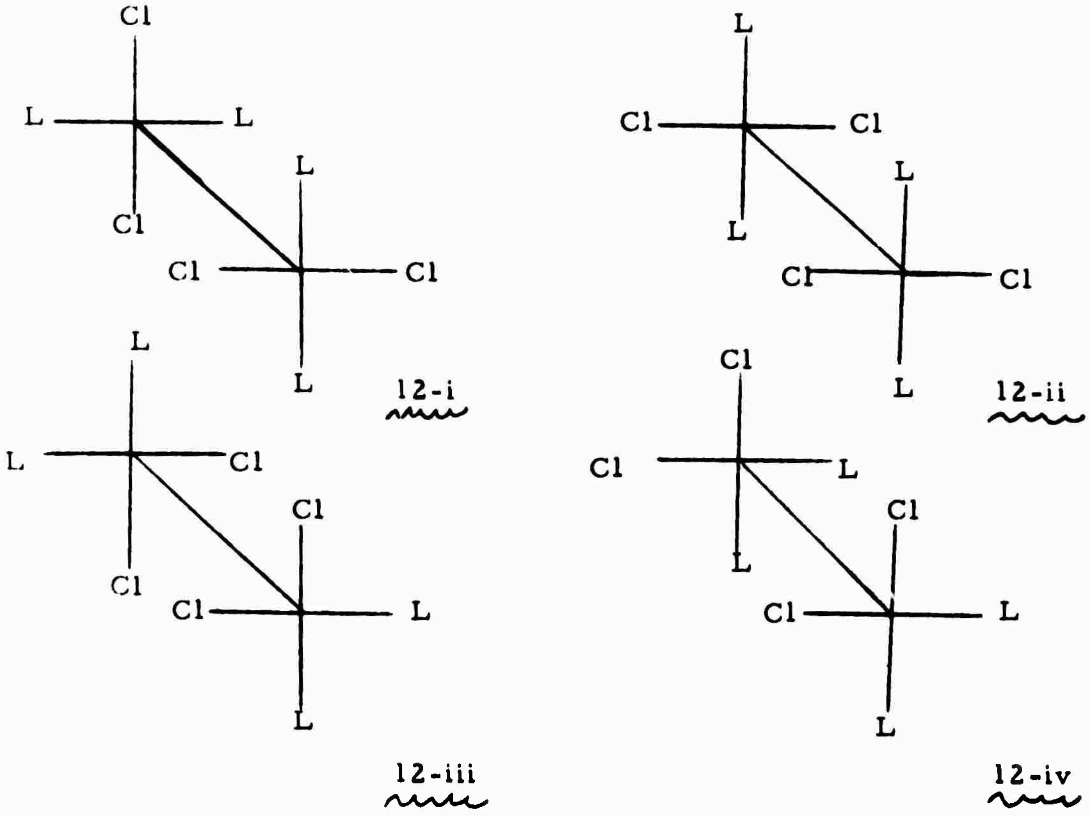
The discussion presented thus far has established that the anamolous deshielding observed in the proton nmr spectra of various complexes proposed to contain multiple metal-metal bonds are explicable in terms of diamagnetic anisotropic shielding produced by the axially symmetrical arrangement of electrons at the metal-metal center. This argument would be strongly enhanced if it could be demonstrated that a similar effect did not result in an analogous effect in a system in which the metal-metal bond was known to be a single σ bond. Unfortunately, systems which at present are recognized to contain a single metal-metal σ-bond, eg. bisdimethylglyoximato(triphenylphosphine)rhodium(II), are not readily modified to an arrangement of ligands in the radial manner, ie. at right angles to the metal-metal axis, as would be required for a valid comparison with the dirhenate(III) or dimolybdenate(II) systems.

Some final observations concerning the 'H nmr spectra of these complexes are noteworthy. The down-field methylene resonance observed in the tri-n-butylphosphine derivatives showed considerable broadening, exhibiting a width at half-height of ~20 Hz. Such broadening is probably the result of strong spin-spin coupling of 'H with the ^{31}P nucleus, superimposed on the usual second order proton-proton coupling of the butyl chain. Quadrupole broadening as a result of spin-spin coupling of 'H with the naturally occuring high spin ($\underline{S}$ = 5/2) isotopes of rhenium ($^{185, 187}Re$, 100%) or molybdenum ($^{85, 87}Mo$, 25%) would not appear to be of any significance in these instances since a similar broadening was not observed in the spectra of the analogous triethyl derivatives.

Attempts to achieve proton-proton decoupling by double irradiation techniques were only partially successful. While such experiments indicated that strong coupling was involved, complete decoupling was never obtained, hence coupling constants could not be assigned. Heteronuclear (^{31}P) decoupling would have been most desirable but was not available.

Complexes 12a-d present an interesting problem in stereochemistry. The similarity between the method of preparing these complexes and that employed to prepare 6a-c, when taken together with the demonstrated isostructural relationship which exists between octachlorobis(tetra-n-butylammonium)dirhenate(III), the precursor to the phosphine complexes 6a-c, and nonachloropentaammoniumdimolybdenate(II), the precursor to the phosphine complexes 12a-d, strongly suggest that the phosphine ligands in 12a-d are equally divided between the two molybdenum centers, ie. two on each. Any other arrangement would necessitate that these ligands be in non-equivalent environments, a requirement which, barring accidental magnetic equivalence, is not substantiated by their 'H nmr spectra.

In light of these considerations, Figure 4 illustrates the likeliest structures for 12, as viewed looking down the molybdenum-molybdenum bond.



12-i **12-ii** **12-iii** **12-iv**

Figure 4.

These structures pose two additional questions. First, what is the disposition of ligands at each metal center? Second, what is the disposition of these ligands towards the ligands on the adjacent metal center? The first question can be resolved by examining the 'H nmr spectrum of the phenyldimethylphosphine and trimethylphosphite complexes of tetrachlorodimolybdenate(II).

The phenomenom of virtual coupling between chemically equivalent, trans oriented phosphorus nuclei in metal-phosphine complex is well documented.[12] Because of such coupling the methyl resonance observed with ligands such as $PhMe_2P$ and $(MeO)_3P$, which appears as a sharp 1 : 1 doublet in *cis* substituted complexes or in the free ligand itself, becomes a distinct 1 : 2 : 1 triplet when these ligands occur *trans* to each other in a phosphine-metal complex. The fact that the methyl resonances of both tetrachlorotetra(phenyldimethylphosphine)- and -tetra(trimethylphosphite)dimolybdenate(II) appear as single, distinct triplets (J = 4.0 Hz and 6.0 Hz, respectively) is consistent with a *trans* arrangement of these ligands on the same metal center as shown in **12-i** and **12-ii**. These results exclude, therefore, **12-iii** and **12-iv** as possible structures; they do not permit an unambiguous choice between the two remaining structures, **12-i** and **12-ii**.

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[12] J. Shaw, *Nature*, 184, 562 (1959); *ibid*., 186, 233 (1960).

Experimental Section

General. Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Magnesium sulfate was employed as a drying agent unless otherwise stated. Nmr spectra were determined on Varian T-60 or HA-100 spectrometers. Chemical shifts are reported in parts per million relative to internal tetramethylsilane and coupling constants are in hertz. Infrared spectra were taken in sodium chloride cells on a Perkin-Elmer Model 457 grating spectrometer. Mass spectra were obtained on a Hitachi-Perkin-Elmer Model RMV-6D mass spectrometer. Analytical glpc analyses were performed on Hewlett-Packard Model 5750 instrument equipped with thermo conductivity detectors and Disc integrator. Response factors were obtained with authentic samples. Static nitrogen atmospheres were employed in all reactions involving organometallic compounds.

Diethyl ether was distilled under nitrogen from lithium aluminum hydride before use. Tetrahydrofuran was distilled from calcium hydride under a nitrogen atmosphere. Pentane and methanol (Matheson Coleman and Bell spectral quality) were used without purification.

Triethylgermanium azide was prepared by a procedure similar to that described by West[13] for the preparation of trimethylgermanium azide. Triethylgermanium chloride (5.0g, 25.6 mmol; Alfa Inorganic) was dissolved in 100 ml of anhydrous ether and transferred to a 250 ml separatory funnel. To this solution was added 2.3g (35 mmol) of sodium azide in 75 ml of 0.1 *M* hydrochloric acid. The resulting mixture was shaken for 30 minutes. The layers separated and the aqueous portion extracted with 10 ml of ether. The ether extracts were combined, dried, and reduced in volume under reduced pressure. Fractionation of the remaining solution provided 4.4g of triethylgermanium azide, bp 104 - 108° (30 mm Hz), as a clear, colorless liquid with a pungent odor. It had ir (CCl_4, CS_2) 3360 (ev), 2955(s), 2930(s), 2905(s), 2872(s), 2095(N, vs), 1460(m), 1420(m), 1378(m), 1343(m), 1285(s), 1245(m), 1146(w), 1110(w), 1020(m), 970(w), 780(m), 760(m), 700(m) cm^{-1}. Its nmr (CCl_4) was very similar to that reported for triethylgermanium chloride[14] and consisted of an A_3B_2 pattern centered at 1.10. Glpc analysis on a 4 foot, 1/8 inch UC-W 98 column at 120° indicated < 1% triethylgermanium chloride.

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[13] J. S. Thayer and R. West, *Inorg. Chem.*, **3**, 889 (1964).

[14] K. M. Mackay and R. Watt, *J. Organomet. Chem.* **6**, 336 (1966).

Bis[cyclopentadienyl(dicarbonyl)iron]germanium diiodide was prepared by a procedure similar to that described by Stone.[15] Germanium diiodide[16] (1.61g, 10 mmol) was placed in a 500 ml 1-necked round bottom flask to which was attached a reflux condenser. Benzene (100 ml) was added along with 1.71g (10.0 mmol) of cyclopentadienyl-(dicarbonyl)iron. This mixture was refluxed for 24 hours under a nitrogen atmosphere. After allowing to cool to reeom temperature, pentane (300 ml) was added and the resulting mixture placed in freezer (-30°) overnight. The brown crystals which formed were collected by suction filtration. Yield: 48%. The ir and nmr were consistent with that of the expected product.

Bistriphenylgermanium(bipyridal)zinc(II) has been mentioned briefly without experimental details.[17] The following procedure was

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[15] N. Flitcroft, D. A. Harbourne, I. Paul, P. M. Tucker, and F. G. A. Stone, *J. Chem. Soc.* **A**, 1130 (1966).

[16] *Inorg. Syntheses*, **3**, 63 (1947).

[17] H. M. J. C. Creemer, Ph.D. Thesis, Department of Chemistry, University of Utrecht, 1969 (p. 111).

developed for its preparation.

A 100 ml, 2-necked flask equipped with a Teflon coated stirring bar was flame-dried under a nitrogen flush before introducing 3.1g (20 mmol) of bypyridyl. A nitrogen inlet adapter was placed in on necked and a No-Air rubber septum in the other. Tetrahydrofuran (20 ml) was added by syringe and the contents of the flask brought into solution. With efficient stirring a hexane solution of diethylzinc (16.4 ml, 20 mmol; Ethyl Corporation) was added in one portion by syringe. The solution immediately turned dark red. After stirring for 15 minutes, a solution of triphenylgermane (12.2g, 40.0 mmol) in THF (30 ml) was added. The volume of the resulting solution was then cautiously reduced at $\overset{\sim}{<}$40 mm while maintaining vigorous stirring. As the more volitile components were removed, the temperature of the reaction flask was slowly raised until after 25 min. a pot temperature of 130° was reached. The remaining mixture was heated at 130° at a pressure of $\sim$1 mmHg for 30 min. Upon cooling, the resultant mass was dissolved in 80 ml of THF, filtered and the volume of this solution reduced to $\sim$20 ml under reduced pressure. Upon addition of 200 ml of pentane to this solution an immediate precipitation of orange-red crystals occurred. These were collected by suction filtration and dried under vacuum in a descicator. Bistriphenylgermanium(bipyridyl)zinc(II) is a stable solid which can be handled in air for short periods of time but a capped vial of this material stored in the laboratory atmosphere showed considerable decomposition after two weeks. The solid is soluble in a broad range of organic solvents but reacts rapidly with halocarbon solvents such as chloroform or other materials having functionalities suitable to reaction, eg. carbon disulfide. It had nmr δ (C_6D_6) showing a complex multiplet center at 7.2δ, exhibiting no evidence of a germanium hydride which appears at 5.75δ for triphenylgermane.

The preparation of bis[cyclopentadienyl(dicarbonyl)iron]germanium dihydride was accomplished by a modification of the procedure described by Stone.[15] Bis[cyclopentadienyl(dicarbonyl)iron]germanium diiodide (6.80g, 10.0 mmol) was suspended in 300 ml of THF in a 500 ml flask. A suspension of sodium borohydride (2.0g, 50 mmol) in THF 50 ml was added and the resulting mixture stirred under nitrogen for 15 minutes before adding 15 ml of anhydrous, oxygen-free methanol and continuing to stir overnight. The mixture was then reduced to near dryness on a rotary evaporator before adding 150 ml of a benzene-hexane mixture (10 : 1). The entire mixture was chromatographed under nitrogen over an 18 inch column of alumina (activity 1). The elutent was evaporated to dryness under a reduced pressure of an inert atmosphere. Attempts to sublime the resulting solid as reported by Stone, *et al*, were unsuccessful and the material was used without further purification.

Rhodium(II) and molybdenum(II) acetate were prepared by the convenient procedure described by Wilkinson.[18]

Tungsten(II)acetate. During the course of the investigation discussed above it became desirable to have available the tungsten analogue of molybdenum(II) acetate. Tungsten(II) acetate was prepared in low yield by a modification of the procedure used to synthesize molybdenum(II) acetate. Tungsten hexacarbonyl (10.0g was refluxed in glacial acetic acid under nitrogen for 3 hours. The resulting solution was cooled to room temperature and treated with ether until no further solid precipitated. The solid which formed was suction filtered and transferred to a Soxlet extraction cup and extracted for three days with THF under nitrogen. There appeared at this time $\sim$1g of a yellow solid in the bottom of the extraction pot. Isolated and dried, this substance had an ir (KBr) very similar to that of molybdenum(II) acetate. The nmr ($CDCl_3$) showed only one resonance, a singlet at 2.0δ. Analysis of this material carried out *without* further purification gave C, 17.3%; H, 2.35%. Calc for $C_2H_3O_2W$: C, 16.1%; H, 2.0%.

trans-Dichloro(tetrapyridinato)rhodium(III)chloride was prepared by the method of Gillard, Osborn, and Wilkinson.[19]

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[18] P. Lezzdins, R. W. Mitchell, G. L. Rempel, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc.*, **A**, 3322 (1970); T. A. Stepheson, E. Bannister, and G. Wilkinson, *ibid.*, 2538 (1964).

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[19] R. D. Gillard, J. A. Osborn and G. Wilkinson, *J. Chem. Soc.*, 1951 (1965).

[Bis(tetra-n-butylammonium)]octachlorodirhenate(III) was prepared by the procedure described by Cotton and co-workers.[20]

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[20] F. A. Cotton, N. F. Curtis and W. R. Robinson, *Inorg. Chem.*, **4**, 1696 (1965).

Hexachloro(bistri-n-butylphosphine)dirhenate(III) was prepared by a procedure analogous to that described for the synthesis of the triethylphosphine derivative. To a solution of $[Bu_4N]_2[Re_2Cl_8]$ (1.0g, 0.877 mmol) in methanol (50 ml) was added tri-*n*-butylphosphine (1.0g, 5.0 mmol). The solution changedfrom a deep blue to a dark green almost immediately. After stirring for an additional 30 minutes, the dark-green crystals that formed were collected by suction filtration and rinsed with 10 - 20 ml of chilled (-78°) methanol and finally with 100 ml of pentane. Total yield was 90%. Anal., calc for $C_{24}H_{54}Cl_6P_2Re_2$: C, 28.82; H, 5.40; Cl, 21.32; P, 7.20; Found: C, 28.91; H, 5.26; Cl, 21.63; P, 6.34. Mol. wt. (osmometry in $CHCl_3$): calc, 989. Found, 980.

The nmr of this complex has been discussed in detail (vide supra). The ir of hexachloro(bistri-n-butylphosphine)dirhenate in $CHCl_3$ was indistinguishable from that of free tri-n-butylphosphine in $CHCl_3$.

Dichloro(tetracarboxylato)dirhenate(III) was prepared by the procedure outlined by Cotton and coworkers.[21]

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[21] F. A. Cotton, N. F. Curtis, B. F. G. Johnson and W. R. Robinson, Inorg. Chem., **4**, 326 (1965).

Dichlorobisdimethglyoximatorhodium(III) was synthesized by the method discussed by Wilkinson.[4]

Chlorobisdimethylglyoximato(triphenylphosphine)rhodium(III) was prepared by treating a suspension of $[Rh(dmg)_2Cl] \cdot HCl$ (see above) in methanol containing 1.1 equiv. triphenylphosphine with potassium hydroxide. After stirring overnight, the crystalline product was collected by suction filtration, rinsed with methanol and air dried. $Ph_3P \cdot Rh(dmg)_2Cl$ is largely insoluble in organic solvents and it should be further noted that this procedure is not general in that attempts to prepare analogous derivatives using tri-n-butyl- or phenyldimethylphosphine did not yield the corresponding phosphine complex of $Rh(dmg)_2Cl$.

The synthesis of nonachloropentaammoniumdimolybdenate(II) was performed as described by Cotton.[22]

Tetrachlorotetra(tri-n-butylphosphine)dimolybdenate(II) was prepared by treating a suspension of $(NH_4)_5Mo_2Cl_9$(3.0g, 5.0 mmol) in anhydrous methanol 50 ml at 0° with tri-*n*-butylphosphine (5.0g, 25 mmol). An immediate reaction occurred as evidenced by the rapid color change from bright red to deep magenta. After stirring for an additional 15 minutes at 0°, the mixture was filtered under suction and the dark crystals collected. The crude yield was virtually quantitative. These crystals were washed with 20 - 40 ml of cold (-78°) methanol and dried under vacuum in a descicator. Attempts to recrystalize led only to decomposition. The nmr spectrum of $Mo_2Cl_4(\underline{n}\text{-}Bu_3P)_4$ has been discussed (*vide supra*). *Anal*: Calc for $C_{48}H_{108}Cl_4P_4Mo_2$ C, 50.44; H, 9.52; Cl, 12.43; P, 10.86. Found: C, 5023; H, 9.24; Cl, 12.24; P, 11.20. *Mol. weight*: Calc, 1141.8. Found (Osmometry, $CHCl_3$) 1149. The ir of $Mo_2Cl_4(n\text{-}Bu_3P)_4$ in $CHCl_3$ was virtually equivalent to that of the free ligand in $CHCl_3$.

Tetrachlorotetra(phenyldimethylphosphine)dimolybdenate(II) was prepared in a manner analogous to that described immediately above using 3.0g (5.0 mmol) of $(NH_4)_5Mo_2Cl_9$ and 2g of phenyldimethylphosphine. The product, isolated by suction filtration of the chilled (-78°) mixture,

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[22] F. A. Cotton and J. V. Brencic, *Inorg. Chem.*, **9**, 346 (1970).

was a dark blue crystalline solid, which was soluble in most organic solvents. The ir in $CHCl_3$ was equivalent to that of the free ligand in $CHCl_3$. It had nmr δ ($CDCl_3$) consisting of a complex multiplet centered at 7.2δ (5H) and a triplet at 2.35 (6H). <u>Anal</u>: Calc for $C_{32}H_{44}Cl_4P_4Mo_2$; C, 43.35; H, 4.97; Cl, 16.03; P, 14.00. Found: C, 42.55; H, 47.6; Cl, 16.02; P, 14.23. <u>Mol. weight</u>: Calc. 885.8; Found (osmometry in $CHCl_3$) 867.

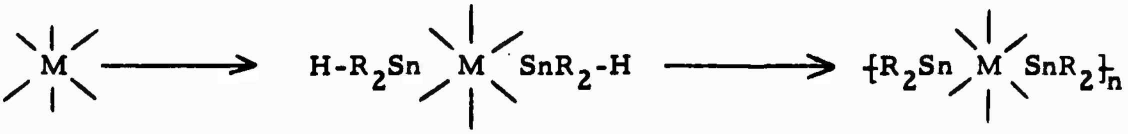
The preparation of <u>tetrachlorotetra(trimethylphosphite)-dimolybdenate(II)</u> and <u>-(triphenylphosphine)dimolybdenate(II)</u> was carried out in a manner exactly analogous to the two procedures described above, except that they were performed under anaerobic conditions. Because of the oxygen-sensitive nature of these compounds analyses could not be obtained. $Mo_2Cl_4(Ph_3P)_4$ is a blue-black crystalline solid, which dissolves readily in chloroform to produce a blue-green solution. $Mo_2Cl_4[(CH_3O)_3P]_4$ was isolated as a dark blue crystalline solid which was quite soluble in most organic solvents.

RESEARCH REPORT

Don Murphy

July 1, 1971

The strategy of synthesizing intermetallic polymers linked by covalent metal-metal bonds has been described in previous reports[1] This reasoning led to synthesis aimed at using the tin hydride-hydrogen elimination coupling reaction (hydrostannolysis) on transition metal systems with tin hydrides in <u>trans</u> positions to prevent cyclization. The general scheme then is,



the transition metal tin hydride coming from reduction of the appropriate transition metal tin halide.

Transition metal tin halides have been prepared in a number of ways: (1) direct synthesis ($R_2SnCl_2 \xrightarrow{\overset{\ominus}{M}Ln} ClR_2Sn - MLn$), (2) electrophilic cleavage of organic groups from tin ($X_3Sn - MLn \xrightarrow[HgX_2]{\substack{X_2 \\ HX}} Cl_nR_{3-n}Sn - MLn$), (3) disproportionation reactions ($2R_3Sn - MLn + Cl_3Sn - MLn \longrightarrow 3ClR_2Sn - MLn$), and (4) Grignard reactions ($Cl_3Sn - MLn \xrightarrow{RMgX} Cl_nR_{3-n}Sn\text{-}MLn$).

The last report describes efforts using the Cobalt bis(diacetylmonoxime-imino)propane 1,3 [$(DOH)_{2\,pn}$] system. We were able to bind organotin groups in <u>trans</u> positions on cobalt with this system (the DOH ligand is tetradentate and must occupy four planar positions), but were unable by any of the means above to obtain any bis halodiorganotin complexes. This led to a reevaluation of other transition metal centers.

By using second or third row transition metals it was felt that the electrophilic cleavage reactions would give desired halodiorganotin species owing to greater tin-metal bond strengths. No second or third row metal centers with a planar tetradentate ligand of appropriate charge was known. Attempts at preparing the rhodium $(DOH)_{2pn}$ system proved unsuccessful. Compounds of the type $(R_3Sn)_2M(CO)_4$ (M = Fe, Ru) had been reported in the literature [2,3]. With iron as the central metal, all compounds were <u>cis</u>, regardless of R. For ruthenium a mixture of <u>cis</u> and <u>trans</u> compounds were formed, ranging from pure <u>cis</u> with R = Me, to pure <u>trans</u> with R = Ph. The Et, Pr, and nBu derivatives were mixed <u>cis</u> and <u>trans</u>. It was hoped that the analogous osmium compounds might strongly favor the <u>trans</u> form. This has proved to be the case, and this report is concerned with that system.

The best way to prepare ruthenium compounds of the type $(R_3Sn)_2Ru(CO)_4$ is the thernal reaction of the appropriate tin hydride and the ruthenium carbonyl cluster [3],

$R_3SnH + Ru_3(CO)_{12} \xrightarrow[\Delta]{} (R_3Sn)_2Ru(CO)_4$. Analogous reactions with Os gave the desired organotin osmium compounds, but also gave a large amount of $R_3Sn\text{-}SnR_3$ as a byproduct from decomposition of the tin hydride. The ditin side products proved impossible to separate from the desired compound, due to similar boiling or melting points, solubility, and retention times on thin layer chromatography. A more satisfactory method of synthesis proved to be the reaction of $Na_2Os(CO)_4$ with the appropriate triorganotin chloride. With Ph_3SnCl the yield is greater than 90% and the product is entirely *trans*. The analogous reaction with $Ru(CO)_4^{=}$ is reported[3] to go in only 6% yield.

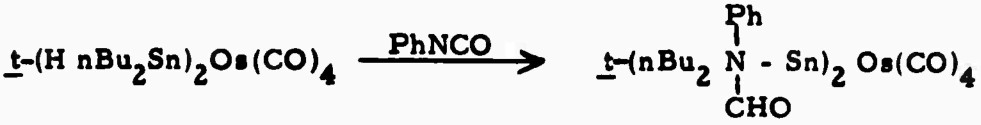
Infrared and Raman spectroscopy were used to determine stereochemistry in this system. *Trans* products have D_{4h} symmetry and thus give only one carbonyl peak in the infrared and two (neither identical to that in the i.r.) in the Raman. *Cis* derivatives are of C_{2v} symmetry and have four CO peaks active in both infrared and Raman. In addition all triorganotin derivatives move on tlc (Si gel), which was used both analytically and preparatively.

Attempts to prepare chlorodiorganotin derivatives directly by the use of the osmium tetracarbonyl dianion gave a mixture of products, difficult to separate. Cleavage reactions proved to be the best way of functionalizing the tin. Stoichiometric treatment of the *t*-$(Ph_3Sn)_2Os(CO)_4$, **1**, with dry HCl gave a complex mixture of products, but excess HCl gave only *t*-$(Cl_2PhSn)_2Os(CO)_4$. Chlorine cleaved the Os-Sn bonds to give *t*-$Cl_2Os(CO)_4$. It is interesting to note that the *cis* isomer of $Cl_2Os(CO)_4$ is the more stable and the isomer given by other routes. Attempts at the disproportionation reaction *t*-$(Ph_3Sn)_2Os(CO)_4$ + *t*-$(Cl_2PhSn)_2Os(CO)_4 \longrightarrow$ 2 *t*-$(ClPh_2Sn)_2Os(CO)_4$ were unsuccessful. A diorganochlorotin derivative was obtained by the selective cleavage of the phenyl groups from t-(Cl $nBu_2Sn)_2Os(CO)_4$, 2. Treating 2 with a stoichiometric amount of diisobutylaluminum hydride in hexane gives the desired monomer unit t-$(HnBu_2Sn)_2Os(CO)_4$, containing trans tin hydrides on a transition metal center.

The stability of this tin hydride is somewhat surprising in view of the fact that no tin hydrides coordinated to transition metals are reported in the literature, and considering the extreme reactivity of supposed di and tri tin hydrides prepared by N. Nelson[7] from $(\pi cp(CO)_2Fe)_2SnCl_2$ and $\pi cp(CO)_2Fe\text{-}SnCl_3$. Dihydrides and especially trihydrides are much more reactive than monohydrides in organotin chemistry, but the difference is not as pronounced as for the cases in point. A model tin hydride, $(CO)_5Mn\text{-}SnPh_2H$, has been prepared to study the coupling reaction. The coupled product, $(CO)_5Mn\text{-}SnPh_2\text{-}SnPh_2\text{-}Mn(CO)_5$, has been reported in the literature[8] having been prepared by an independent route. When the best conditions for the model system is established, they will be applied to the osmium monomer unit.

The stability of the monomer hydride opens up some alternatives in the polymerization reaction. Amides may be prepared from the hydride. The amide nitrogen is subject to electrophilic attack[9] by another tin hydride, $R_3Sn\text{-}NR_2 + HSnR_3 \longrightarrow R_3Sn\text{-}SnR_3 + HNR_2$.

Metal carbonyl hydrides are generally more electrophilic than tin hydrides, suggesting



$$\underline{t}\text{-}(H\ nBu_2Sn)_2Os(CO)_4 \xrightarrow{PhNCO} \underline{t}\text{-}(nBu_2\overset{Ph}{\underset{CHO}{N}}\text{-}Sn)_2\,Os(CO)_4$$

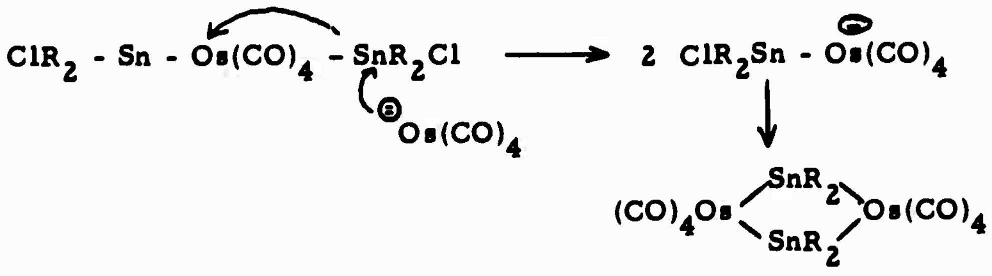
$$\xrightarrow{H_2Os(CO)_4} \left[nBu_2Sn\text{-}Os(CO)_4 \right]_n + Ph\text{-}N(H)\text{-}CHO$$

a route to a polymer of osmium and tin containing no Sn-Sn bonds, considered to be the weak link in the presently planned polymer. The electrophilic reaction is unique among metal metal bond forming reactions in that generally the reactions are nucleophilic in nature.

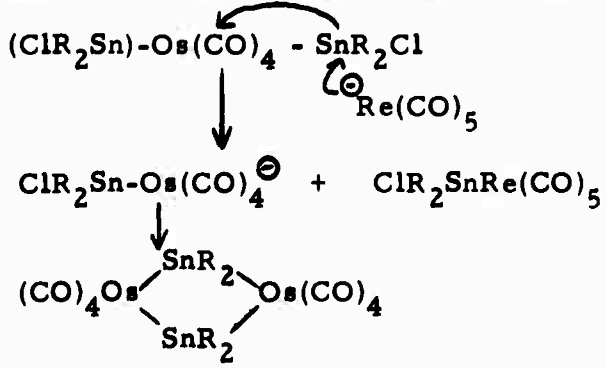
Through attempts to prepare model compounds for X-ray analysis, a new, mild form of the nucleophilic displacement reaction by transition metal anions was discovered. The modification consists of using the corresponding transition metal hydride and generating the anion in the reaction mixture by addition of an inert base, such as an amine. This allows one to circumvent some of the problems associated with using metal carbonyl anions as reagents; (1) anions generally are not pure, and could be termed "reagents", (2) the hydride may be stored and used as required, whereas isolating and storing transition metal anions is quite difficult, especially on a small scale, (3) a wider choice of solvents is available, notably hydrocarbons and benzene. Anion reactions are generally limited to the solvent (usually THF) in which the anion is prepared. The possibility of doing clean nucleophilic displacement reactions suggested a reexamination of its worth as a polymerization reaction. One can write a metathetical reaction of an osmium dianion and a tin dichloride to give a polymer.

$$Os(CO)_4^{=} + R_2SnCl_2 \longrightarrow \left[Os(CO)_4 - SnR_2\right]_x + Cl^-.$$

The reaction (R = nBu), however, proceeds to give a 25% yield of the four membered cycle, 3, where the tins have taken up cis positions on the osmium. Using the preformed trans complex, 2, and the osmium dianion generated from $H_2Os(CO)_4$ in an attempt to preempt cycle formation, still give a 10% yield of 3. A possible mechanism for formation of the cycle is



where the osmium anion attacks the tin in the expected manner, but a dinuclear Sn-Os anion is displaced rather than chloride. To test this hypothesis **2** was treated with the rhenium pentacarbonyl anion generated from the corresponding hydride. This could lead to the cycle via



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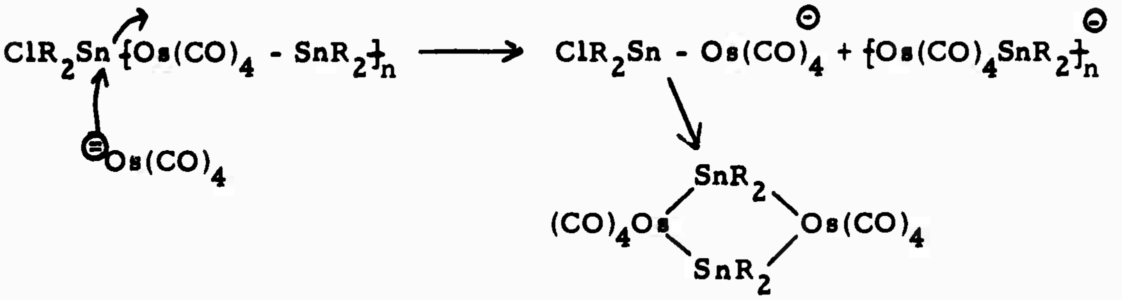
The reaction gave instead the normal product, $\underline{t}$-$((CO)_5Re - SnBu_2)_2Os(CO)_4$. This may imply that the reaction is a chain termination reaction and occurs after some degree of polymerization since polynuclear metal anions are less nucleophilic than mononuclear anions (due to electron delocalization over the entire system) and generally



the weakest nucleophile is excluded in a nucleophilic displacement reaction. If this is the correct explanation, we may be able to circumvent the problem by changing the chloride to a better leaving group and/or a weaker nucleophile.

The main emphasis will continue to be investigation of the hydrostannolysis coupling reaction.

EXPERIMENTAL

dodecarbonyltriosmium[4]

A solution of $OsCl_3$ (3.0g, 61.9% Os) in 50 ml anhydrous ethanol and mossy zinc (1.3g) were heated to 135°C under 1200 p.s.i. CO for 8-1/2 hours in a 300 ml autoclave. The yellow $Os_3(CO)_{12}$ was filtered and purified by soxhlet extraction with CH_2Cl_2. Yield = 2.02g (69%).

disodium tetracarbonylosmium (-II)[5]

The reaction was run in a 3-neck round bottom flask equipped with a dry ice condensor, rubber septum, and tipping tube containing $Os_3(CO)_{12}$. The flask was flushed with Ar and a weighed amount of Na (130 mg, 5.65 mmol) added. About 30 ml liquid ammonia was freshly distilled from sodium into the reaction flask. Osmium carbonyl (715 mg, 2.37 mmol) was then slowly added to the sodium solution, until the characteristic blue color vanished. The ammonia was then allowed to evaporate, leaving a cream colored solid.

trans-bis-triphenyltintetracarbonylosmium, **1**

To the above $Na_2Os(CO)_4$ (2.37 mmol) 25 ml THF (freshly distilled from CaH_2) was added to make a suspension. Triphenyltin chloride (1.92 g, 5.0 mmol) in 10 ml THF was added and stirred 10 minutes. The resulting solution was evaporated. The solid was extracted with benzene and passed through a short silica gel column. The benzene solution was evaporated and the resulting white solid recrystallized three times from CH_2Cl_2 - hexane. Yield = 2.06g (91%).

dihydridotetracarbonylosmium[6]

Solid dianion (5.92 mmol) from 1.787g $Os_3(CO)_{12}$) was pumped on with an oil pump for one hour to remove the last traces of ammonia. The dianion was cooled to -78°C and 35 ml deoxygenated syrupy phosphoric acid added. The flask was placed on a high vacuum line and allowed to warm to room temperature. The clear, colorless hydride was collected in a liquid nitrogen trap, transferred onto 25 g P_2O_5, then transferred into a storage container. Yield = 1.60g (89%).

trans bis(dichlorophenyltin)tetracarbonylosmium

Dry, gaseous HCl was bubbled for ten minutes through a solution of 227 mg (.255 mmol) **1** in 20 ml CCl_4 at -15°C. A white slurry formed. The product was filtered and recrystallized from CH_2Cl_2-hexane. Yield = 110 mg (58%).

trans dichlorotetracarbonylosmium

Chlorine gas was bubbled through a solution of 121 mg (.120 mmol) **1** in 20 ml CCl_4 at room temperature for 25 minutes. A white slurry formed, which was filtered and recrystallized from CH_2Cl_2. Yield = 70 mg (64%).

trans bis(phenyldibutyltin)tetracarbonylosmium

To a stirred slurry of 2.47 mmol of the dianion (made from 740 mg $Os_3(CO)_{12}$) in 30 ml THF, was added a solution of 2.2g $PhBu_2SnBr$ (5.6 mmol) in 15 ml THF. The reaction mixture was filtered and concentrated. Ptlc on silica gel plates (2, 20 x 20 cm plates were used), developing with hexane was used to separate the product from Ph_2Bu_2Sn, a contaminant in the $PhBu_2SnBr$. Ptlc gave product as a clear oil. Yield = 1.50g (66%).

trans bis(chlorodibutyltin)tetracarbonylosmium, **2**

Dry, gaseous HCl was bubbled through a solution of *t* $PhBu_2Sn)_2Os(CO)_4$ (1.50g) in 25 ml CCl_4 at 15°C for 15 minutes. Solvent was evaporated and the product was recrystallized twice from MeOH. Yield = .83g (66%).

trans bis(pentacarbonylrheniumdibutyltin)tetracarbonylosmium

The reaction was performed using vacuum line techniques. Benzene (5 ml) was transferred onto 90.5 mg solid **2** (0.107 mmol), followed by 70.47 mg $HRe(CO)_5$ (0.215 mmoles), and 1 ml Et_2NH. The reaction was stirred 15 min., concentrated and filtered through a short silica gel column with benzene. Removal of the benzene gave the product as a clear, slightly yellow, viscous, nonvolatile oil, which gave one spot on tlc (r_f = .5 in hexane). Yield = 94 mg (55%).

bis μ'dibutyltintetracarbonylosmium, **3**

The reaction was performed using vacuum line techniques. Benzene (3 ml) was transferred onto 277 mg Bu_2SnCl_2 (0.92 mmol), followed by 277 mg $H_2Os(CO)_4$ (0.92 mmol), and 1 ml Et_2NH. The mixture was stirred 2 hours, tlc showed 2 spots very close together at r_f = .6 in hexane. Addition of CCl_4 destroyed one of the spots (presumably a hydride). Concentrating and filtering the resulting solution through a silica gel column with hexane and crystallizing gave the white crystalline product. Recrystallized from Et_2O - EtOH. Yield = 115 mg (23%).

cis-hydridotriphenyltintetracarbonylosmium

To a THF solution containing 1.58 mmol of $Na_2Os(CO)_4$ (from 478 mg $Os_3(CO)_{12}$), 90 ml (1.6 mmol) HOAc was added, followed by 610 mg Ph_3SnCl (1.58 mmol) a large amount of $(Ph_3Sn)_2Os(CO)_4$ was formed in the reaction and ptlc (silica gel developed with hexane - CH_2Cl_2; 85:15) was used to separate the two. Recrystallized from MeOH. Yield = 110 mg (10%).

diphenylhydridotinpentacarbonylmanganese

A solution of $(ClPh_2Sn)Mn(CO)_5$[10] (221 mg = 0.436 mmol) in 5 ml deoxygenated hexane was treated with diisobutylaluminum hydride (436 µl of 1.04 M heptane solution). After half an hour the crude reaction mixture was filtered through an oxygen free silica gel column with benzene. Evaporation and bulb-to-bulb distillation (up to 190°) gave the product as a colorless liquid. Some decomposition at this temperature was observed. Using a molecular still the product could be distilled at 100-120° without decomposition. Yield = 111 mg (55%).

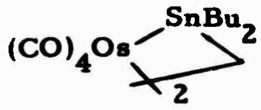
trans bisdibutylhydridotintetracarbonylosmium

The reaction was run as above. The hydride could not be distilled without decomposition, and was purified by chromatography on an oxygen free silica gel column with pentane.

PHYSICAL PROPERTIES

	State	m.p.	i.r. νCO cm^{-1}	RνCO cm^{-1}	RνM-M cm^{-1}
t-$(Ph_3Sn)_2Os(CO)_4$ (1)	colorless solid	222-233	2017 (CH_2Cl_2)	2055, 2111	112 (νOs - Sn)
C - $Ph_3Sn)HOs(CO)_4$	colorless solid	224-225	2120, 2055 2030, 2020(sh) (CH_2Cl_2)	2123, 2057 2038	1946 (νOs-H)
t $(Cl_2PhSn)_2Os(CO)_4$	colorless solid	158-160	2065 2100(wk), 2140(wk) (CH_2Cl_2)	2107, 2163	326 (bd) (νSn-Cl)
t $Cl_2Os(CO)_4$	colorless solid	>300	2075 (CH_2Cl_2)	2127, 2187	327 (νOs-Cl)
t$(PhBu_2Sn)_2Os(CO)_4$	colorless oil		1995(s), 2038(wk) 2078(wk) (hex)		
t $(Cl\,Bu_2Sn)_2Os(CO)_4$ (2)	colorless solid	94.5-96	2025, 2050(wk) 2100(wk) (hexane)		
$[(CO)_4Os\text{-}SnBu_2]_2$ (3)	colorless solid		1999, 2008, 2087 (hexane)	1978(w), 1999 2008, 2087	νM-M 76, 102, 117(wk), 139
$((CO)_5Re\text{-}SnBu_2)_2Os(CO)_4$	lt. yel. oil		1960(wk), 1980(sh), 1990, 2000, 2070 (wk), 2090(m), 2095 (m), 2105(m) (hexane)	2014(wk), 2022, 2031, 2041, 2055(wk), 2112	νM-M 90, 112, 180
$(CO)_5MnSnPh_2H$	colorless oil		2090(s), 2070(m) 2020(m), 1995(s) 1985(sh) (hexane)		i. r. νSn-H 1795 (neat)

ELEMENTAL ANALYSIS

	C		H		Halide		MW	
Compound	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.
t-$(Ph_3Sn)_2Os(CO)_4$ (1)	47.93	47.22	3.02	3.10				
$(Ph_3Sn)HOs(CO)_4$	40.44	40.45	2.49	2.61				
t-$(Cl_2PhSn)_2Os(CO)_4$	23.00	22.95	1.21	1.23	16.97	16.88		
t-$Cl_2Os(CO)_4$	12.81	12.83	0.00	0.00	18.91	18.78		
t-$(ClBu_2Sn)_2Os(CO)_4$ (2)	28.61	28.66	4.33	4.31	8.45	8.17		
 (3)	26.93	26.90	3.39	3.41			1070	1032*
$[(CO)_5Re\text{-}SnBu_2]_2Os(CO)_4$	25.36	25.79	2.55	2.50			1420	1362*
$(CO)_5MnSnPh_2H$	43.55	43.74	2.36	2.34			469	466 ‡

* In chloroform.

‡ In benzene.

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(6) F. L'Eplattenier and F. Calderazzo, *Inorg. Chem*., **6**, 2092 (1967) report the synthesis of $\mathrm{H_2Os(CO)_4}$ by $\mathrm{OsC_4} \xrightarrow[\substack{\text{high pressure}\\ \Delta}]{\mathrm{CO, H_2}} \mathrm{H_2Os(CO)_4}$

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REPORT ON TIN-OSMIUM-TIN DERIVATIVE

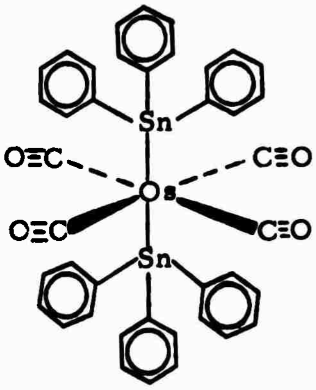
The compound $Os(CO)_4(SnPh_3)_2$ was recrystallized by slow evaporation from hexane to yield a few clear prismatic shaped crystals suitable for x-ray diffraction analysis. A preliminary survey of the crystal with photographic techniques demonstrated that the crystal belongs to the monoclinic system in the space group C2/C (No. 15 Internation Tables). The following cell constants were obtained by a least squares analysis of 2θ data taken on a diffractometer.

a = 47.55 α = 90.00°

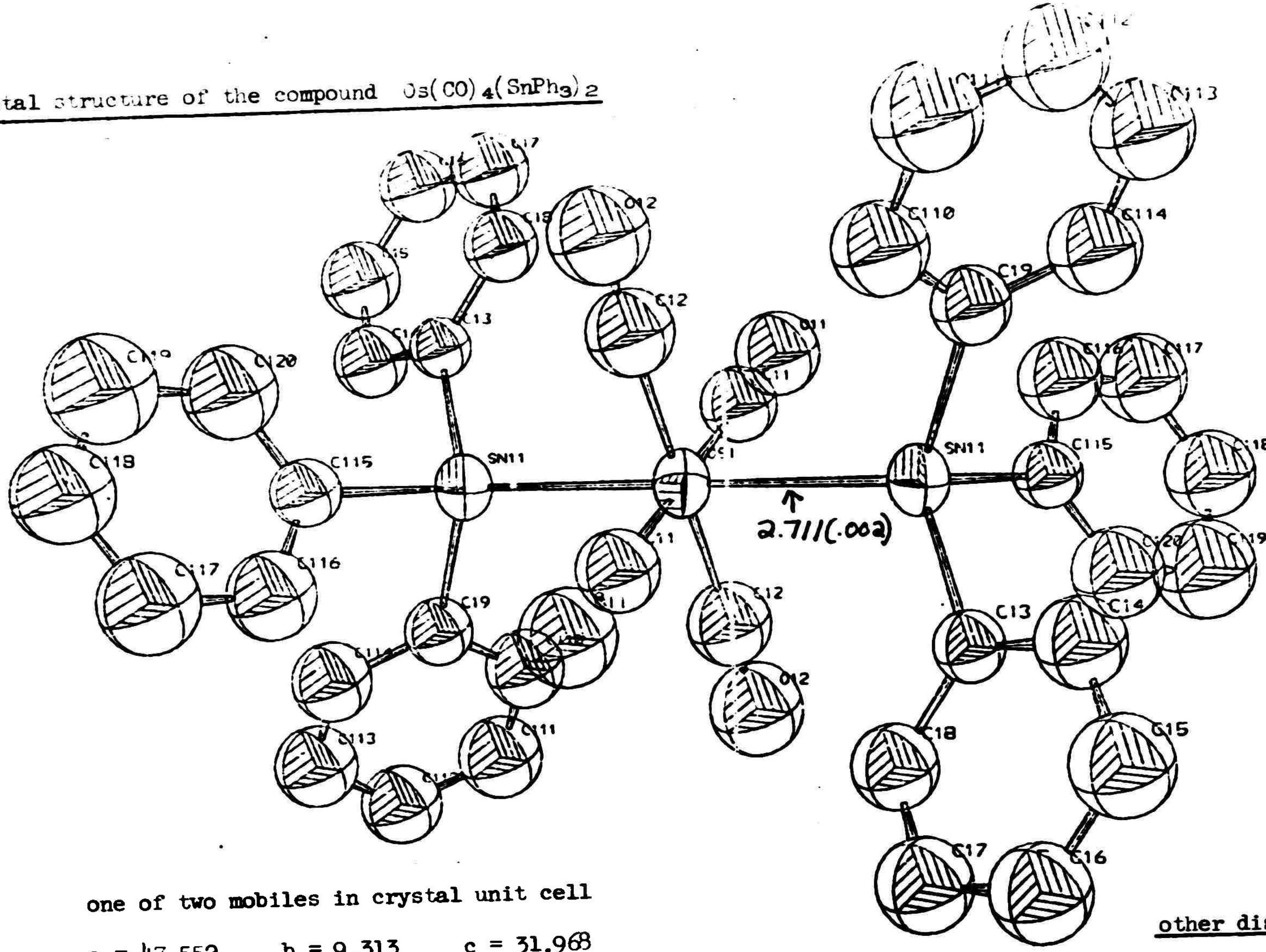
b = 9.31 β = 148.87°

c = 31.97 γ = 90.00°

The measured density allowed for one molecule per asymmetric unit or 8 in the unit cell. A set of diffraction data were collected with a diffractometer MoKα radiation, that was corrected for both crystal decay and absorption. There were 3444 data collected of which 2785 were used as observed (they were 3σ above background as calculated from counting statistics). The structure was solved by usual methods and refined with full matrix least squares to an R-factor of 6.3%. Instead of the molecule lying in a general position in the space group (position f) two-half molecules were in special position (positions b and d) both of which are on centers of symmetry. It turns out that the two independent molecules are very similar in structure. The structure



Crystal structure of the compound $Os(CO)_4(SnPh_3)_2$



one of two mobiles in crystal unit cell

a = 47.552 b = 9.313 c = 31.968

$\alpha = \gamma = 90$ $\cos\beta = -.8560$ $\beta = 148.87$

Space group C2/C

8 Mol/cell (Os on special positions T)

other distance averages

C–C benzene	1.396 (aver. 36)
C ≡ O	1.14 (aver. 4)
Sn–C	2.14_3Å (aver. 6)
Os–C ≡ O	1.90Å (aver. 4)

of the molecule, as shown below, has the following features of interest. The Sn-Os-Sn atoms lie in a line with the angle 180°. The two independent Os-Sn distances, one of the parameters most interesting in the structure, are 2.712 Å and 2.711 Å with an estimated standard deviation of 0.001 Å. All the other distances in the molecule are as one would expect and are all in the normal range--i. e., the 36 C-C distances in the benzene ring average to 1.399 Å; the standard deviation of each individual C-C distance is 0.03 Å. As with any crystal structure, a complete set of atom coordinates and atom vibrational parameters is available.

Since the Os-Sn distance is of most interest in this structure some comment and comparison will be made concerning it. The Sn-Sn distance in four coordinate solid Sn (diamond structure) as 2.810 Å --this leads to a covalent radius of 1.405 Å for Sn; the Os-Os distance in $Os_3(Co)_{12}$ is 2.88 Å [Inorg. Chem. **1**, 521 (1962)] leading to an Os covalent radius of 1.44 Å: This leads to a predicted Os-Sn covalent single bond distance of 2.85 Å. The observed distance of 2.71 Å which is 0.14 Å shorter, indicates some possible double bond or π-bond character of the Os-Sn bond in this compound. Of course, this type of analysis depends on the choice of "standard" covalent distances. If we choose osmium metal instead of the osmium complex to determine the osmium covalent radius, we obtain a radius of 1.34 Å and a predicted Sn-Os distance of 1.75 Å, only slightly larger than the observed distance. Thus some care must be used in the interpretation of bond distances in compounds with little or no available comparative data as in the present case.

IV. EXPERIMENTAL PROGRAM: Physical Measurements

A. Introduction

Our purpose is to characterize the electronic properties of a variety of linear-chain crystals with metal-metal bonds through a series of optical and electrical measurements. These measurements include:

1. Dark conductivity as determined by a 4-point probe method, as a function of crystal orientation, temperature and ambient atmosphere.

2. Thermoelectric power as a function of temperature, ambient atmosphere, and crystal orientation if possible to obtain.

3. Optical absorption throughout the visible and near infrared range (3 - 0.02eV; 0.4 - 50 microns; 25,000 - 200 cm^{-1}) as a function of temperature and polarization of the radiation.

4. Photoconductivity as a function of photon energy, temperature, and intensity.

5. Hall effect measurements on such materials as these may prove possible.

6. Electrical and optical measurements as a function of pressure.

B. Optical Measurements

All optical measurements to date have been made using unpolarized light on $Ir(CO)_{2.9}Cl_{1.1}$, in the form of pressed pellets in KBr. A Perkin-Elmer Model 621 Grating Infrared Spectrophotometer was used for the range from 2.5 to 50 microns, and a Cary Recording Spectrophotometer was used for the range from 0.4 to 3 microns. Typical transmission curves are shown in Figure 1 for two samples with different concentration in the pellet. Detail in the low-energy range is shown more clearly in Figure 2. An absorption threshold at about

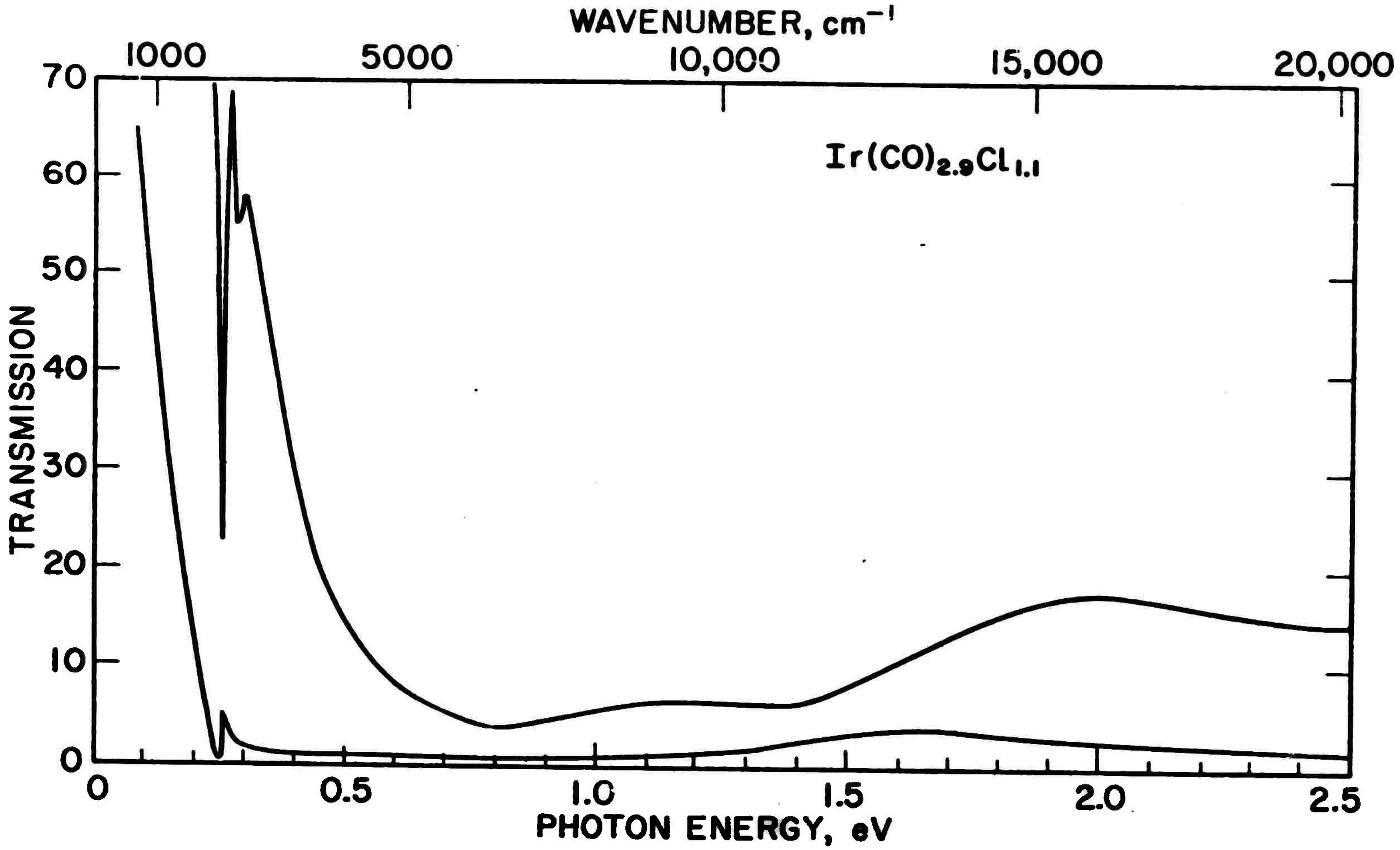


Fig. 1 Infrared Spectrum of $Ir(CO)_{2.9}Cl_{1.1}$ from 0 - 2.5 eV.

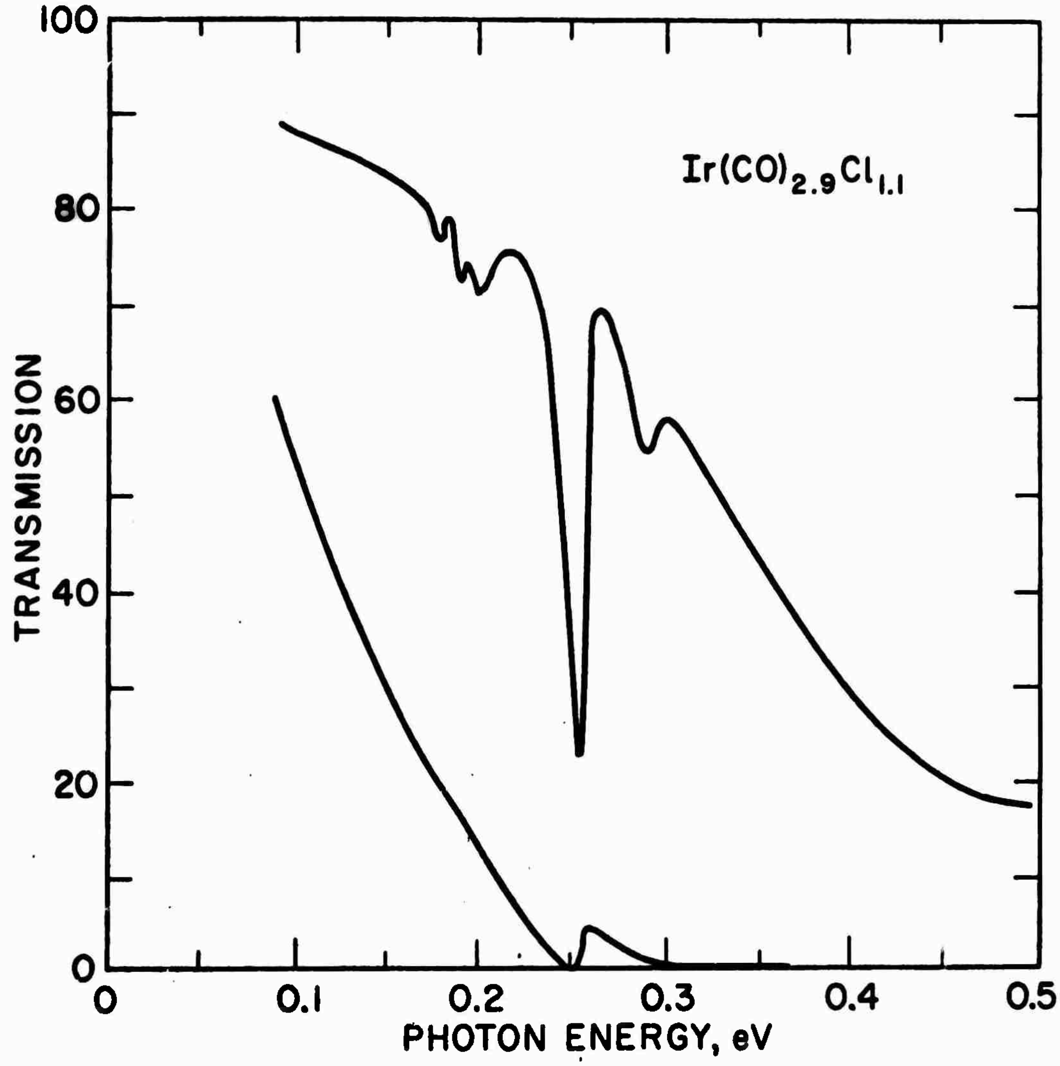


Fig. 2 Infrafed Spectrum of Ir(CO)$_{2.9}$Cl$_{1.1}$ from 0 - .5 eV.

0.05eV is indicated by these data.

C. Conductivity

Summary of Results for $K_2Pt(CN)_4Cl_{0.3}$

Most of the conductivity measurements to date have been made on the material $K_2Pt(CN)_4Cl_{0.3}$. Typical data are summarized in Table I. The data show the importance of 4-point as compared to 2-point conductivity determinations, and also the variable nature of the conductivity for this materials as a function of ambient atmosphere. The first measurements listed for each sample in Table I are made within an hour after the crystal has been removed from a saturated solution.

Result for $Ir(CO)_3Br$

A single 4-point measurement of conductivity on $Ir(CO)_3Br$ gave a value of $3.2 \times 10^{-4}(\text{ohm-cm})^{-1}$, which compares to a value of $6.9 \times 10^{-5}(\text{ohm-cm})^{-1}$ calculated from a 2-point measurement on the same crystal.

Results for Ir (p-toluidine)$(CO)_2Cl$

A 2-probe measurement (Fig. 3) of the conductivity of Ir(p-toluidine)$(CO)_2Cl$ gave a value of $2.1 \times 10^{-6}(\text{ohm-cm})^{-1}$ using aquadag contracts. It also yielded a semiconductor energy gap of (.27 ± .03) electron volts. The observed conductivity is found to be lower by the substitution of (p-toluidine) for a (CO).

Dependence on Contact Material

We encountered considerable difficulty in attempting to use metallic contacts with these materials. In the only case in which the contacts were electrically ohmic, the contact resistance was about 25 times the sample

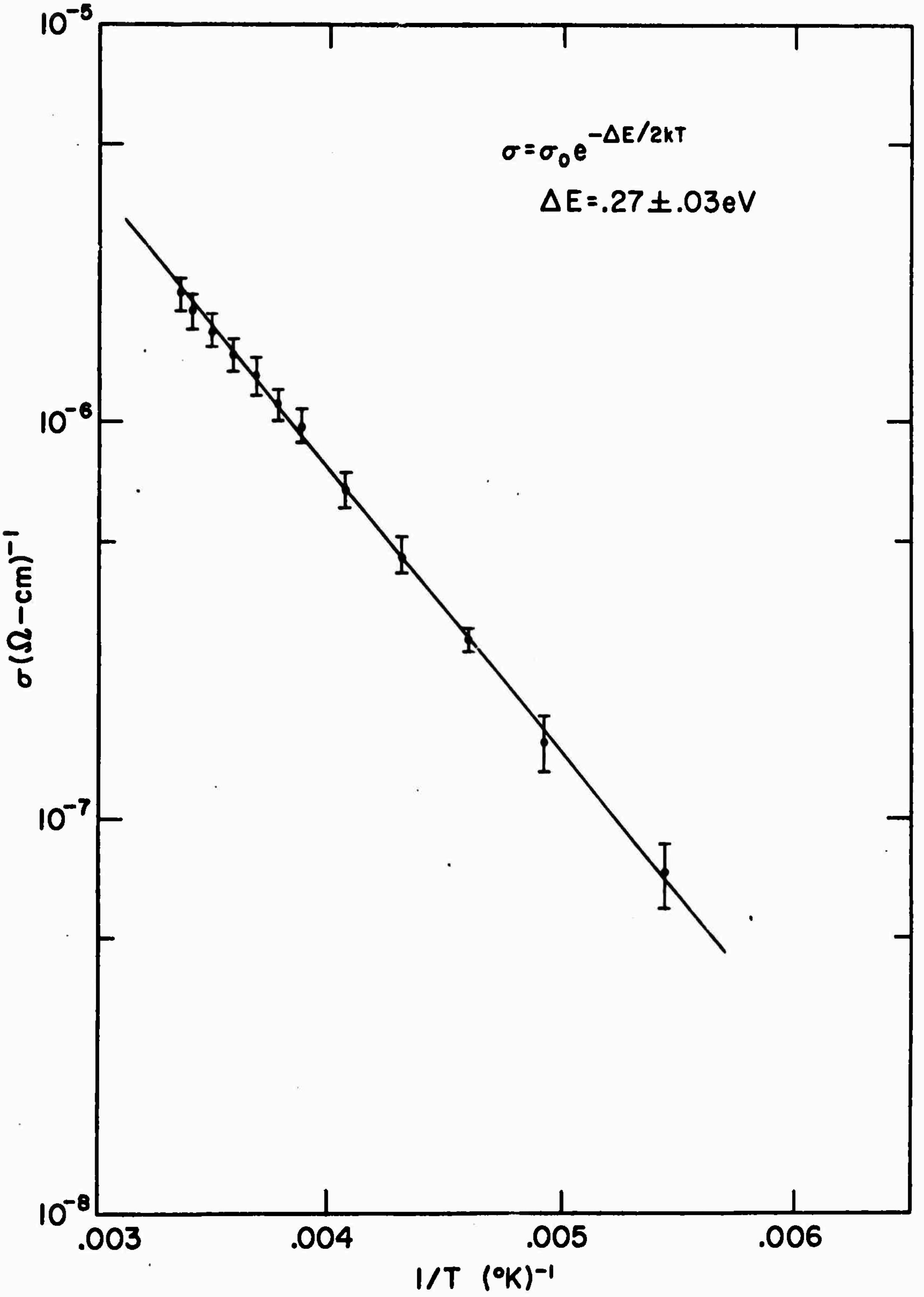


Fig. 3 Conductivity of Ir(p-toluidine)$(CO)_2Cl$ as function of inverse temperature.

resistance; these results were for $Mg_xPt(C_2O_4)_2$ with In-Ga contacts, giving a 4-point conductivity of 0.4 (ohm-cm)$^{-1}$ and a corresponding 2-point conductivity of 0.02 (ohm-cm)$^{-1}$. When used with $K_2Pt(CN)_4Cl_{0.3}$ and gold leads, both In-Ga alloy and silver paste seemed to result in the generation of voltages as high as 0.4 V and to lead to estimated conductivities of 10^{-3} - 10^{-4}(ohm-cm)$^{-1}$. After switching to Aquadag (colloidal graphite) contacts on these same crystals, the apparent conductivities under the same conditions of room temperature and air ambient were in the range 1 - 100(ohm-cm)$^{-1}$. In-Ga does not wet the samples, and silver paste wets only slightly; the Aquadag has a strong tendency to wet the $K_2Pt(CN)_4Cl_{0.3}$ and will dissolve it if applied in too dilute a form.

Dependence on Ambient Atmosphere

The dependence of the conductivity on ambient atmosphere varies greatly between different materials. As shown in Table I, the conductivity of the $K_2Pt(CN)_4Cl_{0.3}$ decreases dramatically upon exposure to a N_2 flush or to vacuum. Data on Sample 4 in Table I indicate an air-conductivity of about 10^4 times a vacuum-conductivity; in one case a ratio of 10^6 was observed. All except for a factor of about 20 seems to be recoverable by allowing air to come in contact with the sample for a long period of time. All of these measurements have been made on samples with Aquadag contacts.

The variation of conductivity with time for the two vacuum runs listed for Sample 4 in Table I is shown in Fig. 4.

It is highly attractive to associate the reversible conductivity of this crystal, which is so ambient dependent, with ionic conductivity, leaving a value of 0.003(ohm-cm)$^{-1}$ as more representative of electronic conductivity.

TABLE I

Conductivity Measurements on $K_2Pt(CN)_4Cl_{0.3}$

$(\text{ohm-cm})^{-1}$

Sample No.	Four-Point Measurement	Two-Point Measurement	Remarks
1	200	0.5	In air
2	32	0.65	Initial
	4.9		1 day later
	0.16		After N_2 flush
3	21	0.016	Bad end contact
	9.3	0.23	Repaired end contact
4	53	4	Initial
	2.4 0.0038		In vacuum next day
	0.01	0.019	After N_2 flush
	0.0035	0.0070	In vacuum again
	0.025		Next day after leaking to atmospheric pressure
	0.246	0.186	After 5 days in air
	0.27 0.0035	0.197 0.0065	In vacuum

TABLE II

Pellet Conductivity Measurements

		$\sigma(\Omega\text{-cm})^{-1}$
1.	4-Chloropyridine Complex	1.2×10^{9}
2.	TCNQ Der. 4-Chloropyridine	.3
3.	$K_{1.8}Pt(C_2O_4)_2$	1.8×10^{-6}
4.	$Ir(CO)_3Cl$	1.8×10^{-6}
5.	Ir (p-toluidine)$(CO)_2Cl$	$\sim 1 \times 10^{-9}$
6.	KNi (biuridium)$_2$	4×10^{-9}

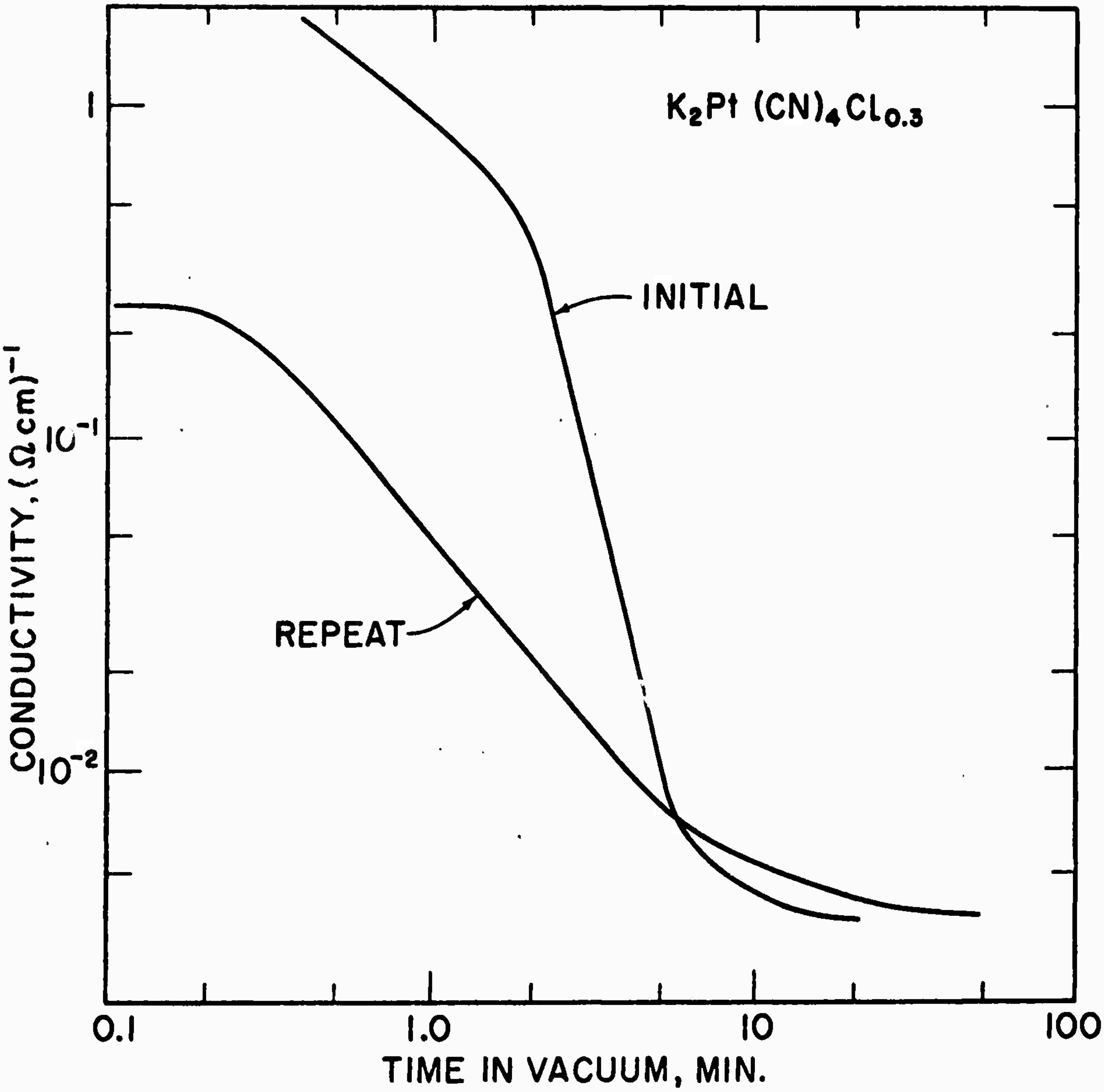


Fig. 4 Conductivity of $K_2Pt(CN)_3Cl_{0.3}$ as a function of time in vacuum.

By contrast to $K_2Pt(CN)_4Cl_{0.3}$, the conductivity of $Ir(CO)_3Br$ is completely unaffected by changing the ambient of the crystal from air to vacuum.

Evidence for Electrolysis of $K_2Pt(CN)_4Cl_{0.3}$

If one passes a current through crystals of $K_2Pt(CN)_4Cl_{0.3}$, under an atmosphere of air, the positive electrode of the crystal is observed to turn to a grayish color. For instance a crystal of width .2mm and length 1.5mm turns gray for about half its length if 6 volts is applied and 1.4×10^{-3}C is allowed to flow. Subsequent analysis of the crystal using electron microprobe techniques shows that the potassium content of the crystal is uniform but that the chlorine content on the gray side is zero. If one runs at a lower voltage (.5 volts) and total charge $.5 \times 10^{-3}$C, no change is observed. This suggests that some electrolytic conduction is occurring.

Pellet Measurements

Often it is useful to provide chemists with information on the electrical properties of compounds before they go to the trouble of trying to make single crystals. To this end a number of 2-probe pellet measurements have been made. Though the absolute numbers obtained are not very useful because they differ from single crystal measurements by a factor of 10^2-10^4, the relative values do give useful feedback information. Table II lists several such measurements.

D. Thermoelectric Power

Thermoelectric power measurements have been made at and near room temperature for samples of $K_2Pt(CN)_4Cl_{0.3}$ in air, and for $Ir(CO)_3Br$ in vacuum.

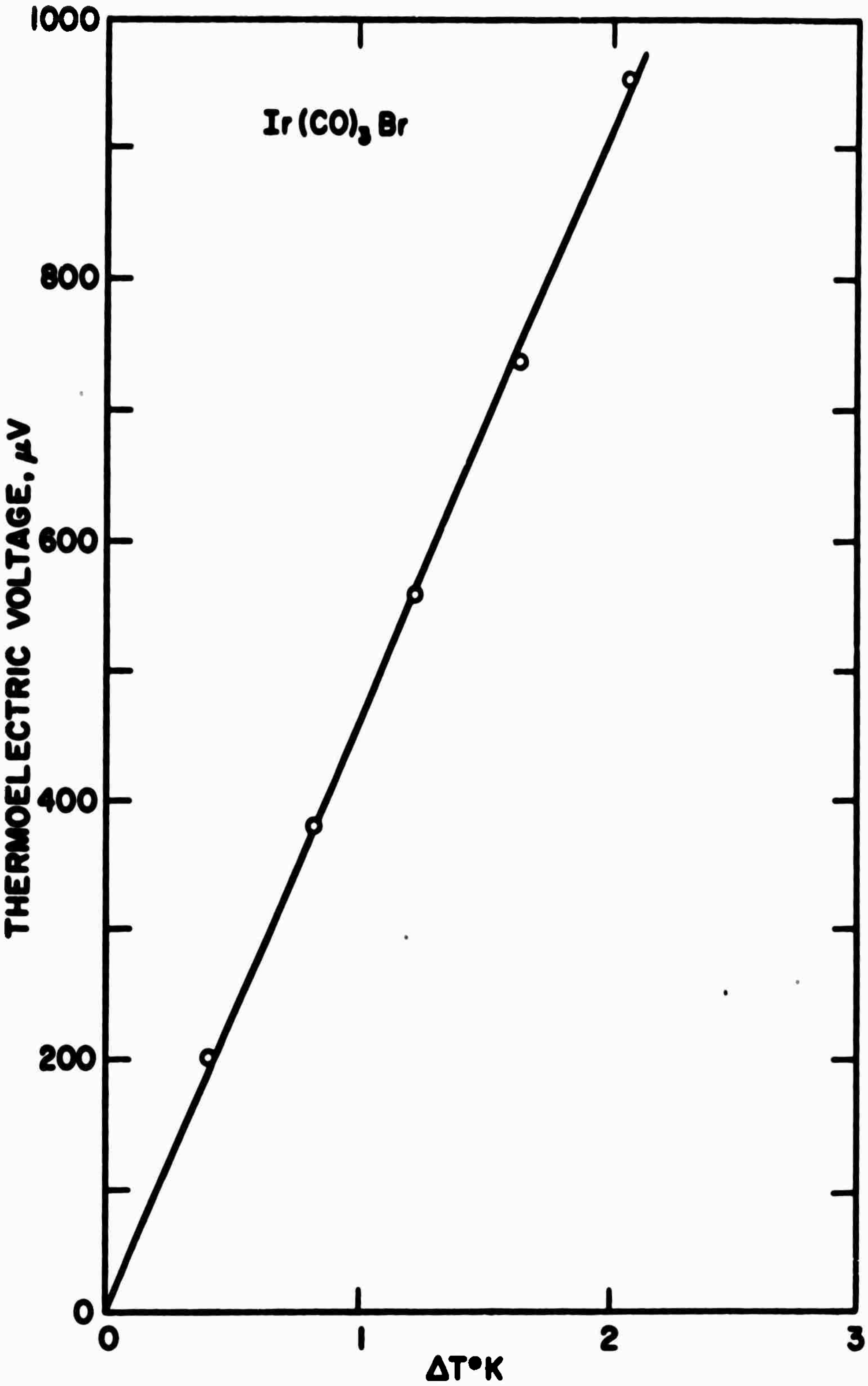


Fig. 6 Thermoelectric Voltage of Ir(CO)$_3$Br as a function of temperature difference.

The dependence of thermoelectric voltage on the temperature difference established across the sample for $K_2Pt(CN)_4Cl_{0.3}$ at 20[illegible]°K and 2[illegible]1°K is shown in Fig. . The voltage axes for the two temperatures have been displaced in order to compensate for a change in voltage-offset for zero impressed temperature difference. It is evident that the thermoelectric power is independent of temperature over this small temperature range, and is equal to 22.6 microV/degree. The sign of the thermoelectric power is positive, implying conductivity by a positively-charged species. The magnitude of the thermoelectric power is sufficiently small that it would correspond to a degenerate semiconductor or a metal, if the species involved were electronic.

The dependence of the thermoelectric voltage on the temperature difference established across the sample for $Ir(CO)_3Br$ at 300°K is shown in Fig. 6. The thermoelectric power is again positive, and for this material equal to 440 microV/degree. This value is sufficiently large that semiconductor interpretation may be justifiable. Because of the independence of the conductivity of this material on the ambient atmosphere, it was possible to measure the thermoelectric power in vacuum from 2[illegible]6°K to 324°K. Over this range, the thermoelectric power is essentially temperature independent, corresponding to a temperature independent carrier density. The dark conductivity (2-point measurement), the carrier density derived from a semiconductor interpretation of the thermoelectric power, and the mobility deduced from these two quantities (assuming that the entire cross-section of the crystal is conducting uniformly) are plotted as a function of temperature in Fig. 7. The dark conductivity has an apparent activation energy of 0.24eV, the carrier density of about $4 \times 10^{1[illegible]}$ cm^{-3}, and the mobility varies from [illegible] $\times 10^{-4}$ to 4×10^{-3} cm^2/V-sec with an activation energy of 0.24eV. Application of a suitable geometrical factor to take account of the fact that the conductivity is primarily along metal-metal chains, and

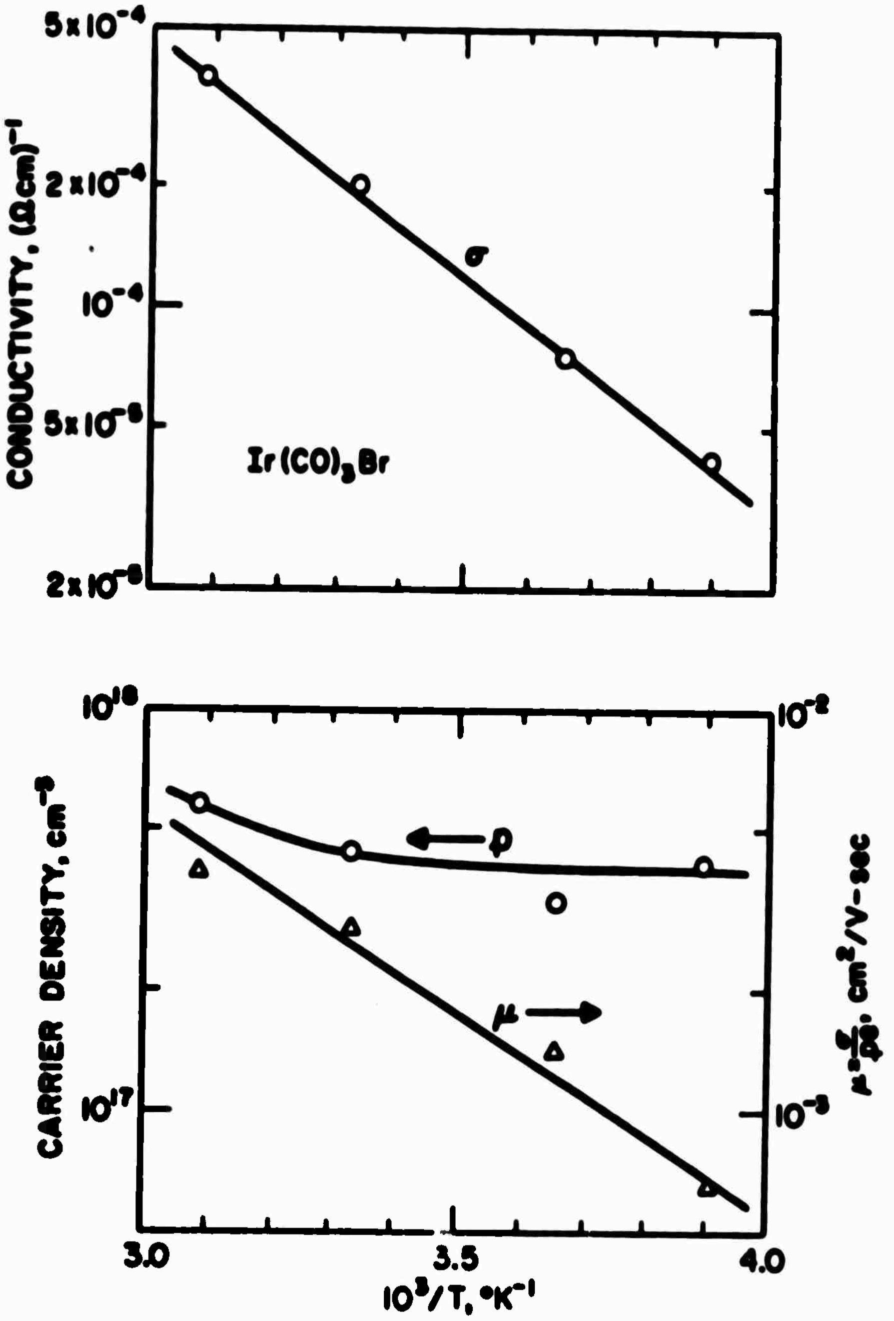


Fig. 7 Top: Conductivity of Ir(CO)$_3$Br as a function of inverse temperature

Bottom: Carrier density (circles) and mobility (triangles) of Ir(CO)$_3$Br as a function of inverse temperature.

not uniformly throughout the crystal, will give an appreciably larger mobility.

E. High Pressure Systems

To investigate the properties of materials under pressure two devices are currently in the development stage. The first is a Beryllium-copper gas bomb. It is intended for use in making conductivity measurements on single crystals under pressure from 0-10 kilobars and temperatures from 77°K - 300°K. The bomb uses Argon or Helium gas as a pressure medium; the hydrostatic quality of these gases should minimize the problem of breaking the fragile crystals.

Fig. 4 shows the construction. The pressure lead and the electrical measurement system come in from the sides and are sealed by a Bridgeman seal arrangement. This means that a rubber, a lead, a brass and a steel washer are sandwiched between the pistons and the male threaded bolt. The force of the gas on the piston makes the seal. The 1/16" threaded hole in the main body was intended to hold an epoxied sheathed thermocouple. This failed at 4 kilobars and will be replaced with a mechanical seal arrangement.

Electrical conductivity measurements give only a slight glimpse at the physical properties of materials. This leads to the second pressure device which is being developed - a cell for doing infrared measurements as a function of pressure.

This cell will press a pellet of KBr plus a small amount of the sample materials between two pistons. These pistons will have a small hole in the center which will be filled with a fused salt crystal. This will make a path for the light to go through. A nut arrangement holds the piston in place and under pressure. The pressure will be measured by strain guages. This entire system is designed to fit into a commercial spectrometer. Thus the whole system is designed to make convenient measurements of the infrared spectra as a

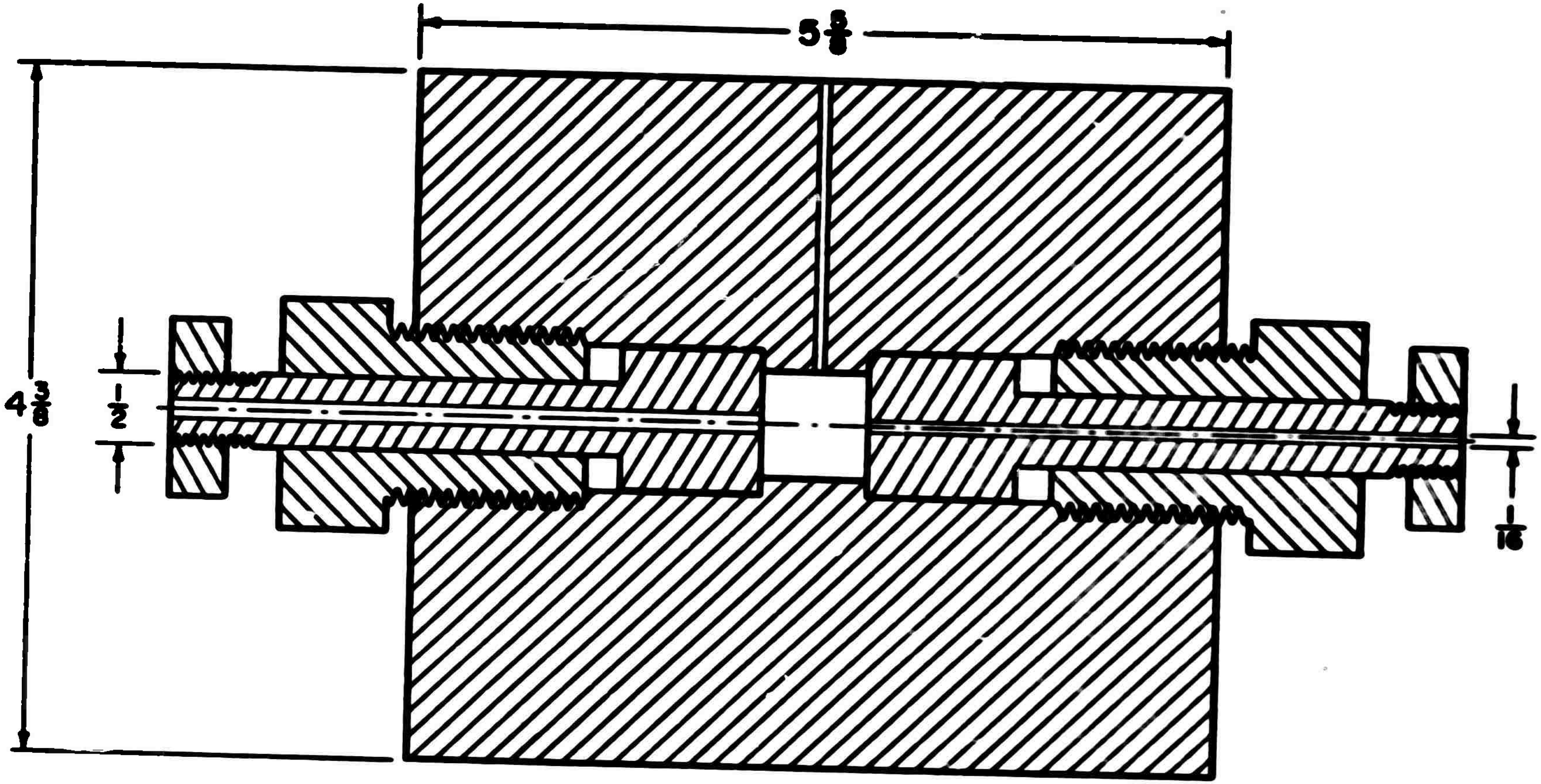


Fig. 8 Drawing for Beryllium-Copper Gas Pressure Bomb

function of the pressure.

Appendix A

The following report describes work during the period April - December, 1970 which was sponsored by the Bonneville Power Administration Contract #14-03-0498N. It is so closely related to the work described in the main body of this semi-annual report that it is included here for reference purposes.

1. Dye-substituted Glyoxime-d^8-metal-Complexes A specific model of a High Temperature Superconductor?

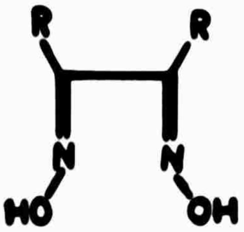
1.1 Introduction

The basic requirement of Little's model for a high temperature superconductor is to have a conducting spine surrounded by a highly polarizable system. (cf. W. A. Little, Phys. Rev., **A134**, 1416 (1964)). The spine was originally proposed to be a long conjugated polyene chain with polarizable subunits (e.g. cyaninedyes) attached to it as sidechains. But these systems proved to be very difficult to handle (synthesis, stability, solubility, determination of the detailed structure of the products, etc.). From this point of view a big step forward was made, at least for the synthetic chemist, when the idea was brought up to use the "linear" interaction of transition metals in some of their square planar d^8 complexes to form the conducting path. This means that one can avoid the difficulties of polymer chemistry as polymerization occurs "automatically" on crystallization of this kind of monomeric complexes. Examples of these d^8 compounds are the "Krogmann's salts" which exhibit a typical semiconductor behavior along the metal chain, (cf. K. Krogmann, Angew. Chemie, i.e. **8**, 35 (1969)), the Magnus' Green Salt, and the red, very insoluble Ni-dimethylglyoxime. Their chemical and physical characteristics (solubilities, color, etc.) are explained by an interaction of the transition metals between adjacent layers, which for many cases was confirmed by X-ray data ("abnormally" small metal-metal distances) and also by visible and u.v. spectroscopy. (For one of the most recent works in this field cf. S. Nagakura et al. Inorg. Chem. **9**, 2551 (1970), Spectroscopic Study of the Interaction between the Central Atoms in Ni-dimethylglyoxime and related compounds.)

Thus, the new task is to find ligand systems to which one can chemically bind the polarizable subunits in a way that these subunits are fixed in a position more or less perpendicular to the metal-metal axis (cf. Little's model). Another possibility would be to electrostatically bind polarizable units to the spine system (e.g. replacing the metal cations in the Krogmann's salts by cyaninedye cations) but the chances of achieving the spatial requirements are very small.

1.2 The model compound

The vic-dioxime system was chosen as chelating unit for the following reasons:



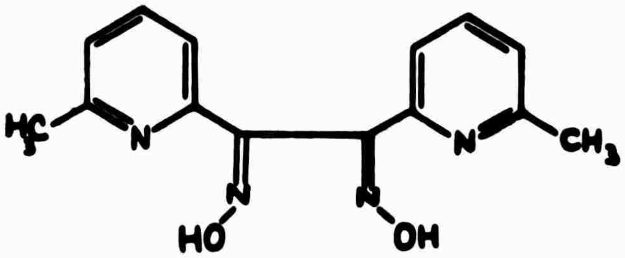
vic Dioxime

a. It is a very strong chelating unit, thus diminishing the danger that the central atom would rather coordinate with the unsaturated sites in the polarizable unit.

b. Replacing $R = CH_3$ in Dimethylglyoxime by other groups (e.g. Phenyl: Benzildioxime; 2-Furyl: Furildioxime; 2-Pyridyl: Pyridildioxime) still gives very stable complexes with Ni, Pd, Pt.

c. Vic-dioximes are often easily accessible via Benzoincondensations (see 1.3).

d. For R = 6-Methyl-pyridyl-2- one has a basic unit on which it was expected to be able to do classical cyaninedye chemistry (see section on problems of the synthesis) and having a tool to tune the polarizable part without repeating the whole synthetic pathway each time to investigate its effect on the conducting chain.



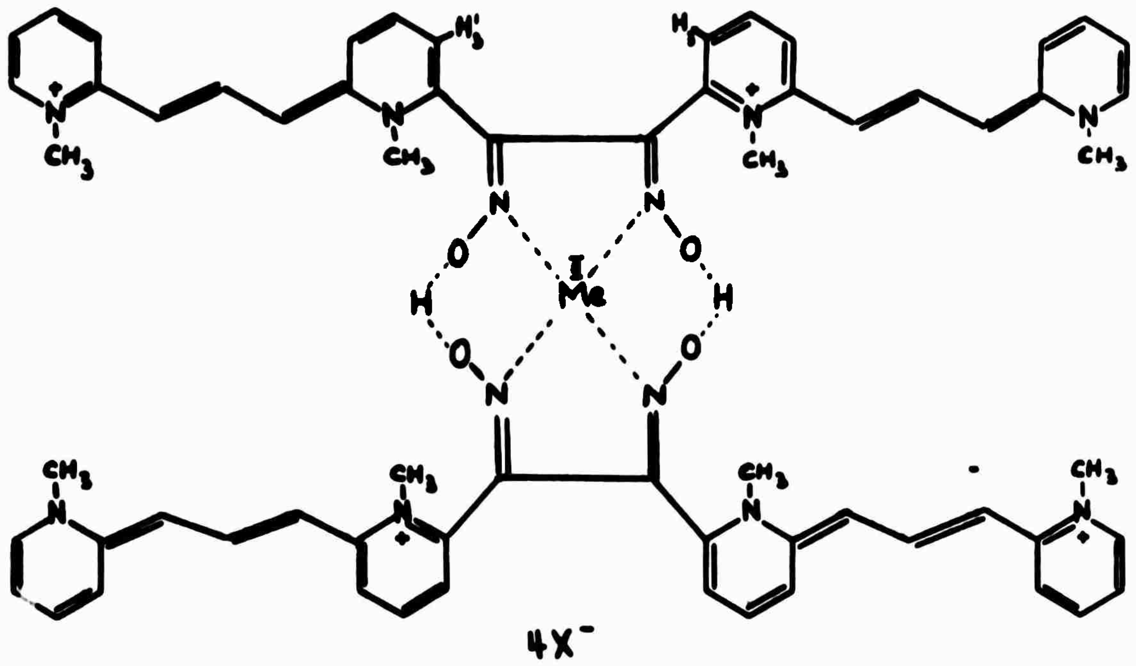
e. As two vic-dioxime units complex with one central atom one can introduce four dye units per metal which might substantially reduce the chainlength of the dye needed as the interaction between dye and spine seems to follow a "linear" behavior in respect to the number of dyes surrounding the metal chain. Simpler cyanine dyes will facilitate handling of the compounds due to greater stability.

As R in the "basic unit", 6-Methyl-pyridyl-2- was chosen for the following reasons:

a. Steric considerations (see below)

b. Though quinolyl heterocycles normally lead to dyes with lower energy absorptions the disadvantage of using pyridyl systems seems to be outweighed by the fact that the oscillating positive charge in the dye is limited to a narrower region and thus making the interaction between charge and spine more effective.

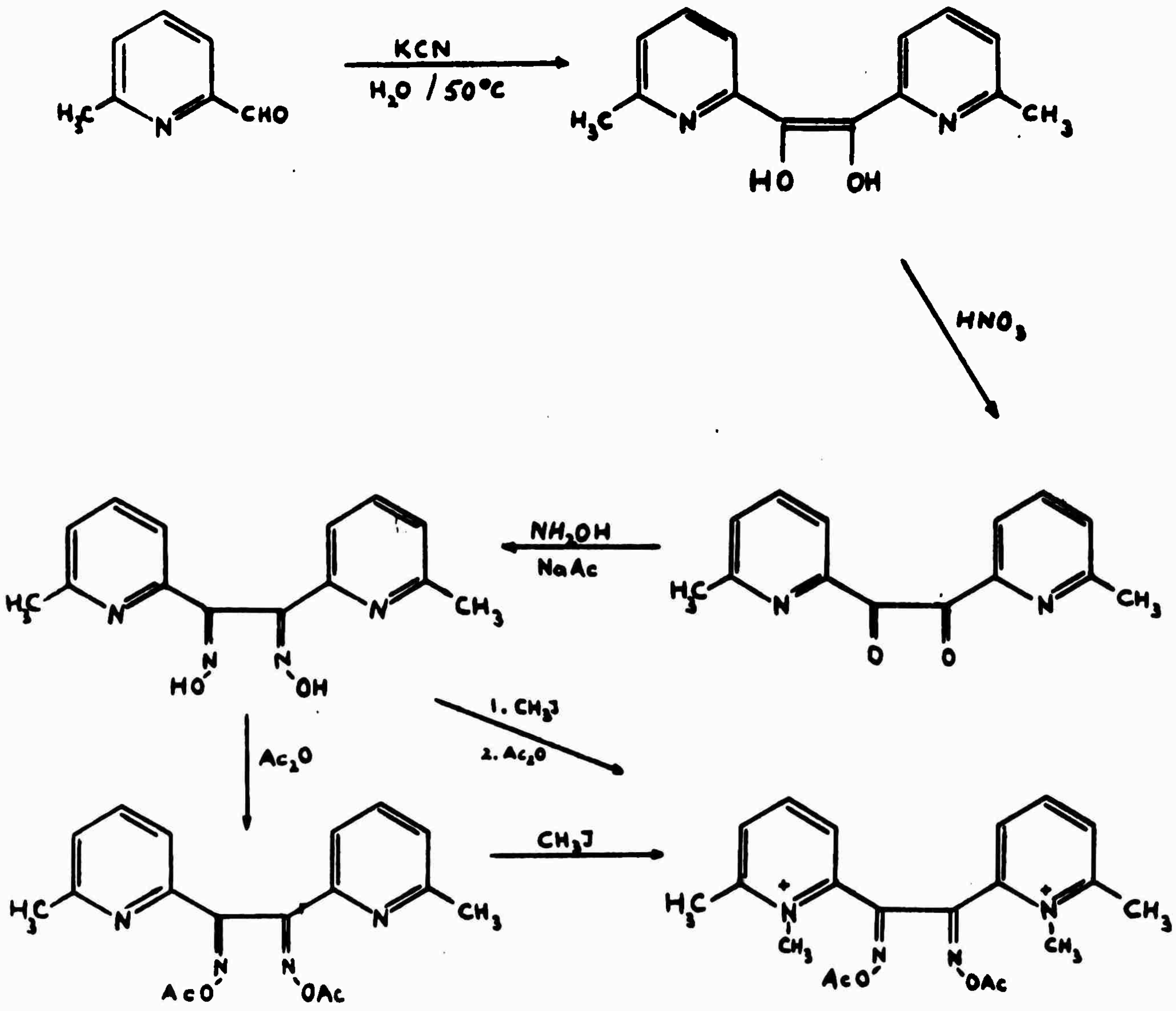
The ideas mentioned up to here led to the proposal of the following compound as a model for a possible high temperature superconductor:

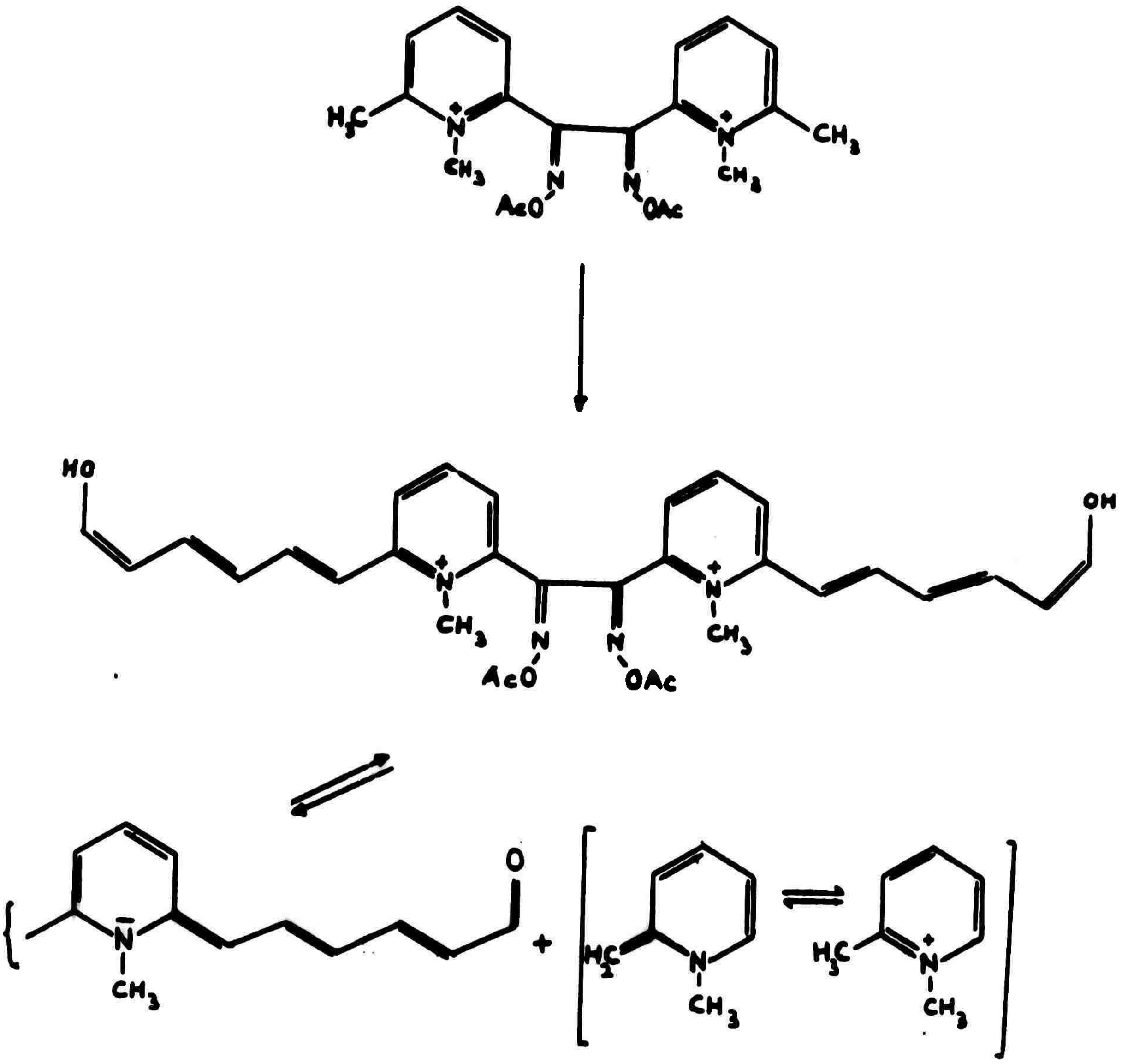


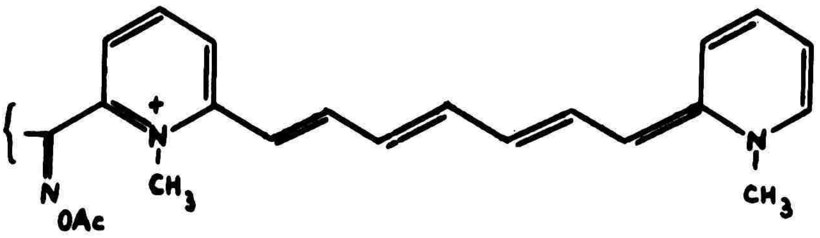
This model is useful of course only is a metal-metal interaction is possible despite the large substituents on the glyoxime. The three dimensional stick models show indeed that with the Pyridyl system, but not with Quinolyl- this might happen as well as it does in Dimethylglyoxime complexes, assuming that there will also be a twisting of each adjacent layer around about 90°, with a metal-metal distance of ca. 3.2Å, as in Ni-dimethylglyoxime. (cf. Ni-dimethylglyoxime X-ray data: L. E. Gadycki, R. E. Rundle, Acta Cryst. 6, 487, (1953)) In fact, there might be even a smaller metal-metal distance possible as the thickness of an aromatic pi-system is less than the diameter of a rotating methyl group. (ca. 3.14Å compared with ca. 3.5Å) In addition the heterocyclic rings on the glyoxime will be torn out of the plane of the coordination due to interference of the H3 and H3' on the rings diminishing the effective thickness in the crystal even further. But, if ever by some reason the above mentioned twisting around 90° should not occur the metal-metal interaction will be very weak as this is the case in the bis(glyoximato) Pt II complex (even without any substituent): Pt-Pt distance 3.504Å. (cf. G. Ferraris et al. Acta Cryst. B 1969, 2066)

1.3 Synthesis

The following route was designed for the synthesis of the above compound:

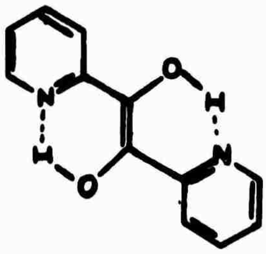






a. Benzoincondensation

The procedure of Harris and Lenart (Ann. 410, 108 (1915)) for the preparation of α-Pyridoin has been used. The reaction goes on very smoothly also in my case using 6-Methyl-pyridin-2-carboxaldehyde, forming 6,6'-Dimethyl-α-Pyridoin in good yield. The product forms orange-yellow needles on recrystallization from hot ethanol, with a melting point of 199°. (reported mp. 198°). Pyridoins reportedly exhibit the en-diol structure (Hensel, Angew. Chemie, 65, 491 (1953)) with strong hydrogen bridges, which might be the reason for the impossibility to quarternize them with methyliodide. (cf. "e")



b. Oxidation of 6,6'-Dimethyl-α-Pyridoin

There are a variety of methods described in the literature to oxidize benzoins. Some of the more recent procedures use e.g. p-toluenesulfonylchloride (Chem. Ber. 91, 1404 (1958), $SOCl_2$ (J. Org. Chem. 27, 2247 (1962)), or Bismuth oxide Bi_2O_3 (J. Chem. Soc. 793 (1951)). None of these reagents were successful, probably due to the en-diol structure mentioned above. So the classical reaction was used with concentrated nitric acid which works perfectly if one keeps some control over the temperature. Whereas Harris and Lenart perform the oxidation by heating the reaction mixture to 100° for three hours (loc. cit. above), here the best results were obtained by adding the nitric acid at 0° and then warming the mixture to 60° for half an hour. Higher temperature and prolonged reaction time lead to an increased formation of an unidentified brown side product.

The product, 6,6'-dimethyl-pyridil (= picolil) forms bright citron yellow needles on recrystallization from hot methanol, mp. 173° (reported 171-172°). Further identification by mass spec.: $M^+ = 240$.

c. Oximation of the Picolil

There are essentially two procedures described in the literature for the oximation of benzil systems:

1. a NH_2OH solution with NaOEt/EtOH and the benzil are refluxed for one hour. (Mary Pitman et al., J. Chem. Soc., 759 (1961))

2. a saturated water solution of $NH_2OH \cdot HCl$ plus the benzil in MeOH are refluxed for six hours. (Chemiker Zt. 37, 773; Chem. Ber. 50, 952) None of these procedures gave satisfactory yields (30% or less). Instead, by using sodiumacetate as buffer increased the yield to 75% or more, giving a white powdery product, which on recrystallization from hot methanol formed colorless plates or cubes, mp. 235°. The formation of a dioxime was confirmed by mass spec. ($M^+ = 270$), and its fragmentation pattern.

d. Acetylation of the Dioxime

As unexpected difficulties arose to quarternize the heterocycle, the dioxime was acetylated because the inhibition of the reaction might have been due to blocking the nitrogens by hydrogen bridges from the oxime groups. A very old and simple procedure is given by K. Auwers and V. Meyer (Chem. Ber., 21, 799 (1888)) to diacetylate dioximes: treatment of the dioxime with two to threefold excess of acetic anhydride at room temperature for 24 hours, or refluxing it for a short time. Surprisingly what was obtained from these reactions was always the monoacetate in yields of about 90%. Even under the more vigorous conditions using pyridine as catalyst only the mono-product was formed. On the other hand again, the hydrogen bridges were not present in Auwers' examples. Heating the reaction mixtures containing pyridine lead to a dark oily product not further identified. But it is well known that vic-dioximes form easily furazanes under dehydrating conditions which might well have happened in this case.

The monoacetate was characterized by its well interpretable mass spec. ($M^+ = 312$). It is recrystallizable from hot benzene, forming short broad colorless needles.

e. Quarternization

No quarternization could be achieved as yet. The literature shows one example of a very similar problem, the quarternization of α-pyridildioxime (Mary Pitman et al. J. Chem. Soc. 759 (1961)) where the dioxime was treated in nitrobenzene under reflux for 18 hours. It is true that in our case the nitrogens are sterically more hindered, but this is even more the case in 2,4,6-collidin which can be methylated under very mild conditions (Chem. Ber. 55, 1356). It is supposed that the inhibition is rather due to an electronic effect (plus steric) the more as 6-methylpyridine-2-carboxaldehyde cannot be quarternized either, but the same reaction occurs very smoothly on its acetal. But the detour over this compound is not successful either because after quarternization acid saponification is completely inhibited due to the positive charge on the nitrogen.(if ever the quarternized aldehyde was stable enough to be isolated).

Other methods tried out used dimethylsulfate, 2,4-dinitrobenzene-methylsulfonate, MeI/Silver sulfate, various solvents such as methanol, nitrobenzene, N-dimethylformamide, chloroform; there was also a series of reactions carried out under pressure in sealed tubes. Quarternizations were also attempted on the pyridoin- and pyridil stage. There will be another attempt undertaken soon starting with 6-methyl-pyridyl-2-methanol, quarternizing it then followed by oxidation and probably direct conversion to the pyridoin derivative.

1.4 Experiments

a. Benzoincondensation

2.4 gr of 6-methyl-pyridyl-2-carboxaldehyde were dissolved in 20 ml of water and a solution of 175 mg sodiumcyanide in 2 ml of water slowly added with vigorous stirring, at room temperature. The 6,6'-dimethyl-α-pyridoin forms immediately and comes out of solution as a bright orange voluminous precipitate. To complete the reaction the mixture is stirred for one hour at 60°. After cooling down to room temperature the precipitate is filtered off, washed several times with water. Recrystallization is best carried out by dissolving the material in as little hot chloroform as possible and then adding hot ethanol until the first crystals form. Yield after one recrystallization ca. 80%.

b. Oxidation of 6,6'-dimethyl-α-pyridoin

To 2.4 gr of the picoloin which was placed in an ice cooled beaker 10 ml of concentrated nitric acid were very slowly added dropwise. A white crystalline precipitate is formed which partly dissolves towards the end of the addition of HNO_3. Then the mixture is kept at 60° for half an hour. After cooling again to ice temperature 50 ml of precooled water is added and the solution neutralized by slow addition of a saturated sodiumbicarbonate solution. This precipitates the product in a voluminous pale yellow form. Filtering and washing with water, recrystallization from boiling methanol yields bright yellow needles (ca. 80%).

c. Oximation of the picolil

1.93 gr of the picolil and 1.2 gr hyroxylamine hydrochloride are dissolved in 40 ml of water and 1.6 gr soldiumacetate is added. The mixture is refluxed for 24 hours. If the yellow color has not disappeared after ca. 18 hours another 1 gr of NaAc is added. Then careful evaporation of the alcohol under vacuum followed by addition of 10 ml of ice cold water which leaves the dioxime as fine colorless precipitate which is filtered off, washed with ice cold water. Recrystallization from hot methanol leaves 1.6 gr (74%) of colorless needles or cubes.

d. Acetylation of the dioxime

100 mg of the dioxime are dissolved in 5 ml of acetic anhydride, leaving it at room temperature for 24 hours or heating it on a boiling waterbath for 1 hour, yields 90% pure monoacetate. The advancement of the reaction can be followed by TLC (silica gel, MeOH/ether 1:1, iodine vapor). No starting material is left after the indicated reaction times. Only one detectable product is formed, although the reaction mixture turns slightly red brown. Recrystallization from benzene yields colorless short broad needles of the monoacetate.

e. Quarternization

No quarternization could be achieved so far on any of the above stages. Methods to detect the quarternary product made use of the expected increased solubility in polar solvents, NMR and mass spectroscopy. Treatment of the dioxime with MeI always yielded a new product on TLC (up to 100%) which could be showed to be probably an iodine complex formed by I_2 liberated during the reaction.

2. Other Systems

2.1 The Krogmann's Salts

Already in 1888 A. Soederbaum (Ber. Dtsch. Chem. Ges. 21, 567) published a report on a variety of intensively colored platinum-oxalate complexes, but his investigations could not reach beyond the stage of a more or less accurate determination of their chemical composition. It was years before Werner derived the concepts of coordination chemistry.

Krogmann recently picked up this class of compounds again using modern analytical methods, primarily x-ray spectroscopy. (cf. Angew. Chemie, i. Ed. 8, 35 (1969)). Though he published the detailed result only of one species ($Mg_{0.82}[Pt(C_2O_4)_2]\cdot 5.3H_2O$), we may assume that others also exhibit the stacked array of the square planar coordinated Pt in the "oxidated" state, for the published Pt-Pt distances vary only slightly (2.80 - 2.88Å). Electrical measurements of some of these compounds showed conductivities up to 10^{-2} ohm^{-1} cm^{-1} in the chain direction. No superconductivity could be ovserved. According to Little this might be due to the following:

These systems probably lie in an energy minimum of the Pt-Pt bond as a function of the Pt-Pt distance. So, no phonon/electron interaction is possible. Eventually such an interaction could be induced by forcing the system out of its minimum by spreading the layers somewhat apart. One means to do this might be the introduction of larger cations, e.g. tetramethylammonium, replacing the metal cations. It was attempted to form the $(CH_3)_4N^+\cdot[Pt(Ox)_2]$. The result of these experiments is the following:

Something similar to Krogmann's Yellow Salts was obtained, as the yellow silver salt was used first and titrated with tetramethylammonium iodide. After filtration of the silver iodide one got a very pale yellow solution which on evaporation yielded a yellowish film on the glass walls. No crystallization could be induced. Addition of some oxidizing agent (Cl_2,-water) produced a dirty greenish brown solution, which, on heating turned to orange yellow but on cooling never gave the characteristic blue color. On cooling, the brown returned. Evaporation, quick or slow, gave a jelly like mass, which did not undergo crystallization. Titration of the free acid (from the yellow silver salt by treatment with HCl) which normally is present in the violet form (due to rapid air oxidation) with tetramethylammonium hydroxide gave directly a yellow brown solution with the same characteristics as described above.

The impossibility of growing crystals of this compound is probably due to the oversized cation (for this system), whose radius of about 6Å, according to the stick model, is more than twice the distance of two layers. On the other hand there is a clear tendency towards polymerization of the Pt-oxalate anions. The "balance" of these two objecting factors seems to lead to the gel like mass, rather than to crystallization of the components in a different arrangement.

Proposal: at this point it is proposed to introduce one of the largest known metal cations as Cs(1.67Å), or Rb(1.47).

In section 1.1, the possibility of binding dye cations electrostatically to the $Pt(Ox)_2^{-2}$ units was mentioned. Two simple experiments were carried out in this regard:

1. Titration of $Ag_2Pt(Ox)_2$ with 1,1'-Diethyl-2,2'-cyanine iodide, with the intention to precipitate the silver iodide, leaving a solution of $Dye_2Pt(Ox)_2$. But on titration the red color of the dye was destroyed, presumably by complexation with Ag^+. No silver chloride was formed.

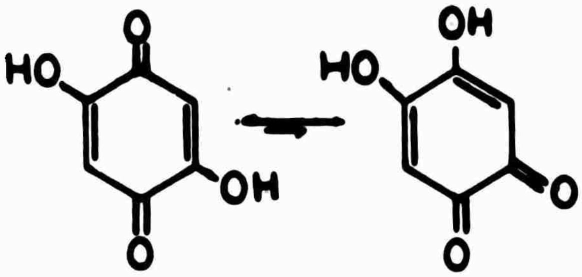
2. This experiment was based on the hope that the $Dye_2Pt(Ox)_2$ might be less soluble than $K_2Pt(Ox)_2$, thus adding a saturated solution of 1,1'-Diethyl-2,2'-cyanine iodide in water to a saturated solution of $K_2Pt(Ox)_2$. On cooling or slow evaporation the two components crystallized separately.

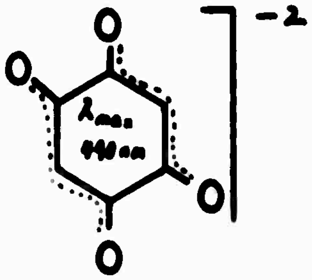
From these two experiments it seems to be necessary to first convert the Dye-I into Dye-OH by a strongly basic anion exchange resin, then titrating the Krogmann free acid with the dye base. This procedure has not been carried out yet.

2.2 A modified Oxalate Ligand (cf. Krogmann's Salts)

Up to now all polarizable entities surrounding the spine in Little's model considered had a positive charge oscillating. According to the calculations this is not a necessary condition. Thus a polarizable medium with a negative charge is equally oportune, expanding the synthetic possibilities somewhat.

The system being attempted at this time may be considered to be an expanded oxalate ligand. It is derived from 2,5-dihydroxy-benzoquinone.





The paraquinoid form might perhaps rearrange to an orthoquinoid one in order to function as a chelating agent, similar to the oxalate dianion. The negative charges are delocalized over to the oxygens in metaposition, so, essentially over the same path length as in the simplest cyanine dyes (e.g. 1,1'-diethyl-2,2'-cyanine, $\lambda_{max} = 522nm$). But of course the free oscillation of the charges is disturbed in the complex by the positive central atom. Yet, there is no direct conjugation between the metal and the organic part, as the complexing orbitals on the oxygens lie orthogonal to the conjugated system. The polarizable unit will be extremely near to the spine (if ever formed) which is a big advantage. Though this ligand is probably not an ideal one in respect to superconductivity, it might give some insight into the spine-polarizable-unit interaction by comparison with the "simple" oxalates.

The experiments done so far yielded dark black-brown powder. No single crystals could be grown. The product is very water soluble, giving a brown yellow color. The reaction was followed by visible spectroscopy, but it is not possible to draw definite conclusions from that. Anyway, the following observations could be made: the di-K-salt of 2,5-dihydroxy-p-benzoquinone has one broad maximum in the visible region at 490nm. The K_2PtCl_4 shows two maxima, one at 470 nm and a 3-4 times stronger one at 391 nm. A 2:1 mixture at room temperature of the two components gives a superposition spectrum. Heating the mixture for 10 minutes to 60°C produces a new spectrum with a completely new pattern. There are no clearly separated maxima (only inversion points) at ca. 520 nm, 405 nm and 360 nm.

Heating the mixture over night gives rise to a steadily increasing absorption starting beyond 900 nm with a maximum around 300 nm. The only detail recognizable any longer is a shoulder at ca. 510 nm.

It is doubtful whether a definite product was formed but further experiments will be carried out.

2.3 TCNQ complexes

Some TCNQ salts exhibit very high conductivity, especially those with the composition $M^{+}TCNQ^{\cdot -}(TCNQ)$, for example M^{+} = Quinolinium: 0.01 ohm-cm on single crystals. Furthermore they show an electronic excitation in the near infrared region (around 3 microns), no paramagnetism in solid state, a variable one in solution (temperature and concentration dependent) (cf. JACS **82**, 6408 (1960), ibid. **84**, 3374 (1962)).

It was intended to prepare a series of such complexes with a variety of cyanine dyes with the purpose to study the effect of the "dye length" on the electrical conductivity and other behaviors. It turned out that by the reaction $\text{Dye } I^{-} + 2TCNQ \rightarrow \text{Dye } TCNQ^{\cdot -}(TCNQ) + 1/2\, I_2$ only the simplest cyanine dye (1,1'-diethyl-2,2'-cyanine iodide) forms a complex salt of the above type, whereas with the higher homologues the dye system is destroyed. From

1,1'-diethyl 2,2' cyanine iodide one gets a nicely crystalline product (dark shiny plates mp 251°). The visible spectrum shows the typical pattern for the $M^{+}TCNQ^{\cdot -}(TCNQ)$ composition, with the dye maximum not affected. The infrared spectrum exhibits the expected electronic absorption in a very broad region (2,5-6 microns) with considerable intensity; it is so strong that the strong CN triple bond stretching absorption of the TCNQ at 2200 cm^{-1} is barely observable. Measurements of the electrical conductivity are under way.

With the next higher vinylogue, the Cryptocyanine, the chromophore is destroyed the same as with 1,1'-diethyl-2,2'-dicarbocyanine, but in the latter case an extremely dark black, charcoal-like, powdery product could be isolated. Its dye peak at 710 nm has disappeared and a new double peak at 610/6[illegible] nm built up. The spectrum further reveals that this is most likely a simple TCNQ salt ($M^{+}TCNQ^{\cdot -}$). This seems to be confirmed also by the infrared spectrum.

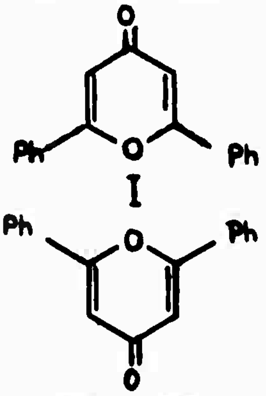
In the meantime, it was discovered that the impossibility to form the more complicated complexes is due to the method of preparation used. The iodine formed in the course of the reaction of the dye iodides with TCNQ is responsible for their destruction. An alternative method to prepare TCNQ complexes is described in the literature (cf. L. R. Melby et al. JACS 84, 3374 (1962), B. H. Klanderman J. Chem. Phys. 51, 377 (1969), J. H. Lupinski, Mol. Crystals 3, 241 (1967)) using Li TCNQ and the dye iodide. (LiI is precipitated; metathesis) This method will be used for further investigations.

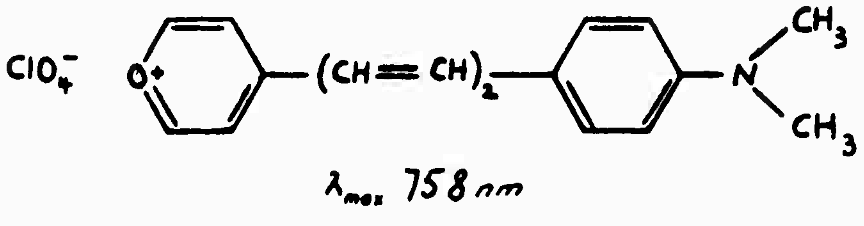
2.4 Cyanine dye iodide/iodine complexes

As can be seen from section 2.3, only the simplest cyanine dyes (e.g. 1,1'-diethyl-2,2' cyanine iodide) are unaffected by iodine. Thus, adding I_2 in chloroform to a concentrated solution of the above dye precipitates shiny golden plates, which can be recrystallized from chloroform/benzene mixtures. The electronic spectrum reveals that there is no interaction of the components in solution. On heating it to 190° I_2 is evolved, at ca. 215° the complex melts with a bright green color, whereas the commercial dye itself does not melt up to 250°, but steadily decomposes above 150°. X-ray and electrical measurements are pending.

2.5 2,6-diphenyl-γ-pyrone and related compounds

Cramer (Chem. Ber. 84, 859 (1951)) describes the formation of an Iodine inclusion compound with 2,6,-diphenyl-γ-pyrone, with the iodine included between the two phenyl groups. As far as it was found there is evidence given for a polyiodine structure, but not for the claimed arrangement of the environment. It is doubtful whether there is any continuous chain at all (private communication by V. Hadeck). But if so, and if the carbonyl group was replaceable by a highly polarizable medium this kind of compound could be useful for our purposes, according to Little. There is indeed a class of compounds known with high polarizability, e.g.:





(cf. M..H. Palmer, Heterocyclic Compounds, Edward Arnold (Publishers) Ltd. London 1967, pg. 211)

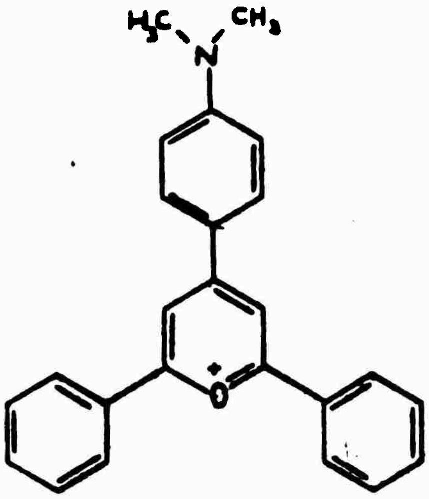
To learn something generally about the complexing behavior of pyrylium salts against iodine, a much simpler substance was used first, the 2,4,6-triphenyl-pyrylium, which is very smoothly formed by the reaction of two moles acetophenone with one mole acetaldehyde in the presence of acetic anhydride and with the calculated amount of $FeCl_3$ (sublimed) as catalyst. This gives $FeCl_4^-$ as counter ion (cf. Houben-Weil, Sauerstoff-Verbindungen I, pg. 355 (1965)). The product is a nicely crystalline substance of an orange yellow color and a characteristic blue, very intense fluorescence in solution. On addition of KI/I_2 solution to a hot water solution of the complex salt a highly insoluble brown-red precipitate is formed immediately which on recrystallization from hot ethanol yields a mixture of red and blue-black needles. On standing at room temperature the red needles change to the same dark color as the others. Renewed recrystallization of the dark form leads again to a mixture of the two forms at first. Thus, this phenomenon is obviously related to the existence of two isomorphic appearances of the substance. Further investigations (primarily x-ray analysis) are pending.

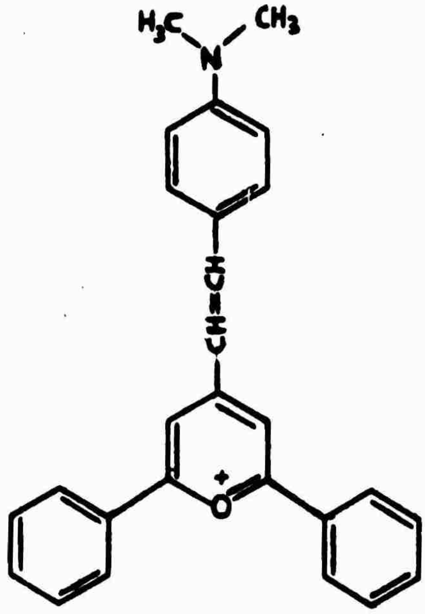
A compound related to the γ-pyrone, the 2,6-diphenyl-γ-quinopyrane, can be formed by a reaction analogous to the one used for the formation of the previous substance, involving p-Hydroxybenzaldehyde (instead of benzaldehyde itself). At first one gets the 2,6-diphenyl-4-p-hydroxyphenyl pyrylium salt (again with $FeCl_4^-$). Treatment of this compound with a weak base, e.g. sodium-acetate, leads to the intense red chloroform soluble quinopyrane. The deprotonation can be nicely followed in the visible spectra. The acid shows two maxima at 394 nm and 462 nm. The base exhibits a kind of a triplet with maxima at 482, 512 and 548 nm. This is in accord with the data reported by W. Dilthey et al. (Chem. Ber. <u>53</u>, 252 (1920), and B. Froehlich et al. ibid. <u>101</u>, 3990, 4004 (1968)) who prepared the same substance by another route.

Treatment of the acidic form with KI/I_2 again forms a brown precipitate at first which changes its color to orange after some minutes and on attempted recrystallization yields an amorphous orange yellow powder.

Treatment of the base form in the same way leads to a dark brown red oil which could not be crystallized and whose visible spectrum indicates that the quinopyrane chromophore has been destroyed.

Condensing 2 moles of acetophenone with one mole of p-dimethylamino-benzaldehyde, or p-dimethylamino-cinnamicaldehyde should in principle lead to the two polarizable units





again as $FeCl_4^-$ salts. Though on mixing the components the same exothermic behavior as in the previous cases could be observed and intense green and red green solutions respectively were formed, the work-up of the reaction mixture did not lead to a definite product in either case. After evaporation of the acetic anhydride in the vacuum, addition of benzene and extraction with water only pale yellow solutions were formed. This might have been due to a nucleophilic attack of the water on the pyrylium system under ring opening, as it is described in the literature for some cases. But it is surprising with what ease this reaction should have occurred, compared to the two previous examples, especially as the p-dimethyl-amino groups should give a stabilizing effect. It cannot be denied that eventually the complex $[FeCl_4^-]$ is responsible for this behavior as itself might complex with the amino group. Furthermore, it should be pointed out that most examples of these extended systems are reported with the stabilizing perchlorate anoin (some few use Cl^-) but that involves quite a different and much more complicated synthesis.

2.6 A Cyanine Dye Polyvinylalcohol Polyiodide Complex?

It is reported that the Schardinger Dextrins form inclusion compounds with iodine but also with iodine/iodide depending on the procedure. (cf. Dexter French, the Schardinger Dextrins, Adv. in Carbohydrate Chem. 12, 189 (1957)) For example, there is a species known with the general composition (α-Dextrin $I_2)_2KI$. The basic unit seems to be a pair of α-dextrin molecules enclosing an I_5^- ion. The α_2-I_5^- units pack in a hexagonal or pseudohexagonal arrangement which gives an x-ray diffraction pattern with essentially the same spacings and intensities as in the amylose I_2 complex. The observed dichroism indicates that the I atoms are aligned along the needle axis. This means that it is possible to build up a poly-iodine-iodide chain, without a big effect on its behavior compared to the "classic" polyiodine arrangement.

In the case of the polyvinyl alcohol it is possible to form the blue complex either just by treatment of the alcohol with I_2, or by its treatment with KI_3. To my knowledge it is not known whether this leads to a polyiodide complex, or to a polyiodine one, leaving KI in solution. But considering the above mentioned fact makes it likely that the former complex might well be formed. One also has to consider the fact that in these blue complexes the iodine atoms are in a metallic like excited state, thus having the d orbitals well available to incorporate "excess" electrons from Iodides.

Using 1,1'-diethyl-2,2'-cyanine iodide instead of KI might thus lead to a PVA-polyiodide complex surrounded by the dye cations as counterions.

The following experiment was carried out: A PVA/I_2 solution was prepared and its concentration adjusted so that the absorption in a 1 cm cell reads about 30%. A dye solution was prepared with a 90% absorption under the same conditions. Adding dropwise the I_2 complex to the dye solution makes the original dye maximum at 522 nm disappear and build up a new peak at 584 nm. The maximum intensity of the new maximum that can be achieved is the same as in the original dye solution. The side peak of the dye seems to be shifted in the same way. Unfortunately, the movement of the "blue" peak of the PVA/I_2 complex cannot be observed in detail, but one may say that it is undergoing a blue shift (which would be expected in Little's model).

An experiment was carried out semiquantitatively. The extinction coefficient of a PVA/I_2 complex is about 10^4, that of the dye ca. 3×10^4, so that the concentrations of the prepared solution were about 1:1 (moles:moles). The maximum height of the shifted dye peak was reached after an addition of ca. 100% (vol) of the dye solution, then the unchanged peak started to increase. Thus, neglecting the dilution effects, ca. 1 mole dye was complexed to the 1 mole/I_2 in the PVA channel. The dye complex solution shows an interesting optical appearance. If light is falling through the solution it has a blue appearance. If light is falling onto it, it looks red orange (kind of metallic reflection?).

Thus far this polymer has not crystallized and no x-ray or other analysis has been carried out.

2.7 A Silver (0) Polyvinylalcohol inclusion compound?

The work with the PVA/I_2 raised the idea whether it might be possible to include a true metal instead of the metal like iodine into polyvinylalcohol. For the selection of the metal there will be essentially two factors to be considered:

a. the size of the metal atom in its (0) state must be in the same range as iodine (1.4Å) to fit into the PVA channels.

b. the metal must initially be present as a watersoluble salt to form a homogenous mixture with a water solution of PVA. Thus, reduction of the metal ions is required (eventually in the channels). Chemical reduction would not be favorable because of two reasons: 1. such a method forms a bulky transition state, eliminating a priori the possibility of a reduction in the channel, making diffusion of individual atoms into the channels necessary; 2. even the slowest chemical reduction would occur at such a high rate that the concentration of metal (0) would be so big that crystallization of the metal would occur (though perhaps only micro crystals would be formed). But, of course, this definitely would inhibit the incorporation into the PVA. These two conditions practically limit the choice to silver, which can be very slowly reduced by light. Keeping the initial mixture in the dark for some time would allow a good deal of the small Ag^+ (1.25Å) to diffuse into the channels, where they might be reduced and locked (Ag^+: 1.44Å) to form a one dimensional "wire." Indeed, exposing a mixture a 5% PVA solution containing ca. 50% (weight; in respect to PVA) of $AgNO_3$ yields a transparent blue solution after exposure to daylight for several days. The intensity of the color is much less than in the case of the iodine inclusion compound, but its absorption maximum lies at lower frequency, at 670 nm. The appearance of the absorption curve is very similar to the one with iodine (broad "round" band).

Adding much more silver nitrate to the PVA solution also produces the same blue solution at first but on prolonged exposure to light the system begins to become opaque, remaining blue with light falling through but exhibiting a greyish color with light falling onto it.(compare end of section 2.6). Centrifuging this solution at ultra high speed gives a grey precipitate (still blue in a very thin layer?) and the solution itself turns clear and colorless. Whether this precipitate consitutes free silver, or a complex, has not yet been established.

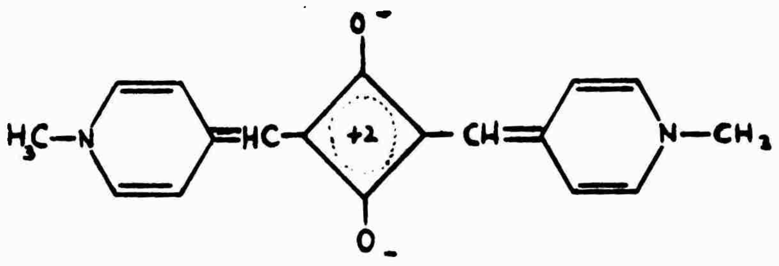
To determine whether an inclusion compound has been formed it will be necessary to prepare stretched films and record their x-ray pattern. But it is expected to still be difficult to distinguish between a true inclusion compound, or microcrystals aligned by the stretching process.

The occurrence of light polarization and dichroism will neither tell anth thing about which of the two possibilities is actually present as either case will exhibit these effects (in the stretched form) (cf. optical anisotropy of metallic surfaces; gold microcrystals in PVA films; V. N. Lebedeva et al. Dokl. Akad. Nauk. SSSR <u>167</u>, 556 (1966)).

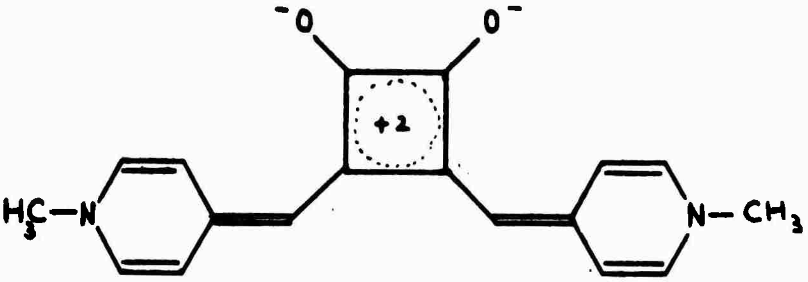
2.8 A proposal for a squarylium dye metal complex

No experiments have been carried out yet in connection with the below proposal.

Two kinds of nucleophilic substitutions are known on the squarylium system. Starting with squaric acid leads to 1,3- substituted products, e.g.



Starting with the squaric acid diesters gives the 1,2- substituted forms, e.g.



These latter systems might behave similarly towards d^9-metals as the oxalate anion. In respect to their complexability I would expect them to be much more favorable than the system proposed in section 2.2 as the negative charges will be rather localized on the oxygens to prevent the destruction of the atomaticity of either the four or six membered ring. Hence, the affinity of the ligand towards the metal cations will be much greater.

These ligands exhibit very high oscillator strength at reasonably low frequencies, thus fulfilling an important condition for Little's model. They are planar and of about the same thickness as the oxalate. They will allow the polarizable part to reach very near to the spine. There will be four polarizable units surrounding one metal atom.

A disadvantage of this system will be that there is no simple way to tune it, i.e. to very the length of the polarizable part (lit. on squarylium dyes, cf. among others H. E. Sprenger, W. Ziegenbein, Angew. Chemie. 79, 581 (1967)).