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NEW SUPERCONDUCTORS

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Stanford University

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February 1 - July 31, 1972

NEW SUPERCONDUCTORS

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13. ABSTRACT

This report covers work on the study of possible high temperature superconductors. It described theoretical work on filamentary organo-metallic materials - the conduction mechanism, band theory, and screening; progress towards the synthesis of metallic chain compounds and related organo-metallic complexes, and experimental studies of their solid state properties.

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TABLE OF CONTENTS

I. INTRODUCTION

This report outlines the work and progress of a program aimed at obtaining a better understanding of the problem of achieving superconductivity at higher temperatures. It is a coordinated program involving the study of the synthesis of new materials, the analysis of their physical, chemical and structural properties coupled with a closely knit theoretical program. The program to date has concentrated on two main classes of compounds, the Krogmann compounds which are mixed valence transition metal stacked organo-metallic compounds and true covalently bonded metallic polymers. Studies have been made of the synthesis of organic ligands to which polarizable dye-like structures can be attached. From developments in these areas of synthesis, information is fed back into the program of theoretical studies modifying the choice of the most suitable systems.

In the course of the past six months an important development has occurred in the synthetic program which has important consequences for the theoretical program and for the program as a whole. Drs. Mayer and Winkler have prepared cyanine-dye bases and have shown that these can be complexes directly to a transition metal transforming at the same time the cye base into a true dye. The significance of this lies in the fact that the polarizable dye can be brought into intimate contact with the conductive spine formed by the chain of metal atoms. This has two effects: first, the resultant excitonic interaction becomes substantially larger than for alternative configurations where several bonds separate the ligands from the dye; and, secondly, the close proximity increases the range in momentum space over which the excitonic interaction is significant. The latter point has been stressed by Bulayevsky and Kukharenko (Preprint 49, Lebedev Physical Institute, 1971) as being of great importance for any significant enhancement of T_c.

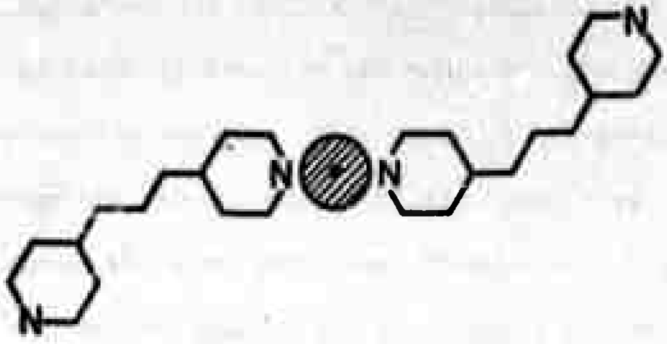
The details of the synthetic work are given in the section by Mayer and Winkler, while the theoretical consequences are discussed in the next section.

II. THEORETICAL PROGRAM

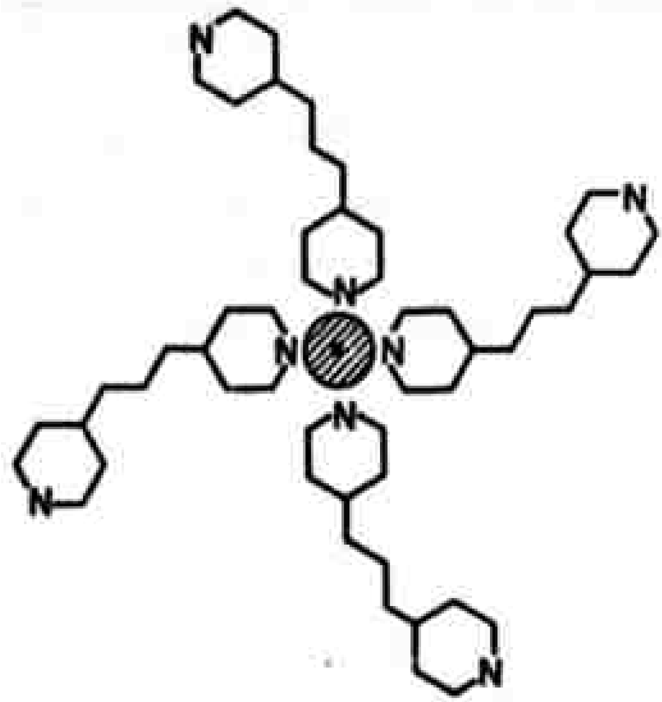
As described in the previous report a first approximation to the solution of screening in filamentary compounds was obtained by Duane Davis. A paper on this has been accepted for publication in the Physical Review. Using those results as a guide we have been able to extend our earlier calculations of the excitonic interaction in stacked transition metal compounds with polarizable side chains to the situation where the Coulomb interaction is screened. The method of calculation is identical to that described in our first annual technical report except that the bare Coulomb interaction is replaced everywhere with a screened interaction of the form $(a/r)\exp(-\kappa r)$ where $\kappa = 0.14\text{Å}^{-1}$ as estimated by Davis.

The calculations have also been extended to two new structures which the work of Mayer and Winkler suggest may be possible to prepare. They have shown that the nitrogen of one half of a cyanine dye can be complexes directly to a metal and that the metal then effectively quarternizes the nitrogen. It is reasonable therefore to consider structures of two or four dyes complexed to a metal as illustrated in Fig. 1. These structures appear not to be hindered sterically except perhaps in so far as stacking is concerned. A point to which we will return later.

Our results are shown in Fig. 2(a) and 2(b). In 2(a) we show the excitonic interaction as a function of momentum transfer q for electrons assumed to be located in a "spine" perpendicular to the plane of the dyes and with a metal-metal spacing of 3.4Å. In the dye-glyoxime system considered earlier the four dyes in the unit cell are some distance from the metal chain because of the glyoxime attaching unit. This both weakens the net interaction as can be seen in comparing it with the results of the proposed four



2-DYE STRUCTURE



4-DYE STRUCTURE

Fig. 1 Proposed two and four dye structures using Mayer-Winkler dyes.

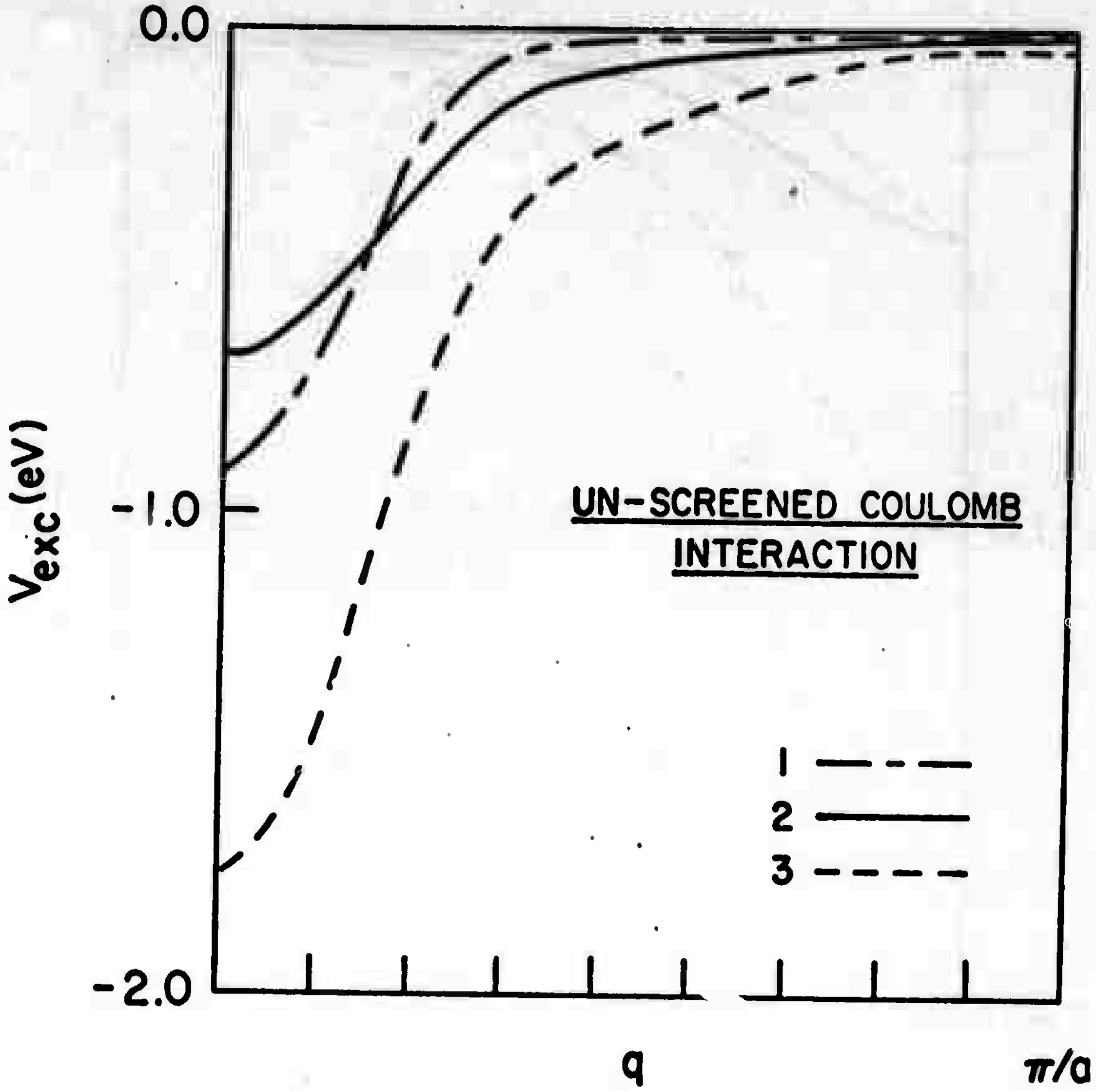


Fig. 2(a) Excitonic interaction as a function of momentum, q, calculated with an unscreened Coulomb interaction.

1 - the four-dye glyoxime structure (Fig. I-1, First Annual Technical Report)

2 - the two dye structure of Fig. 1

3 - the four dye structure of Fig. 1.

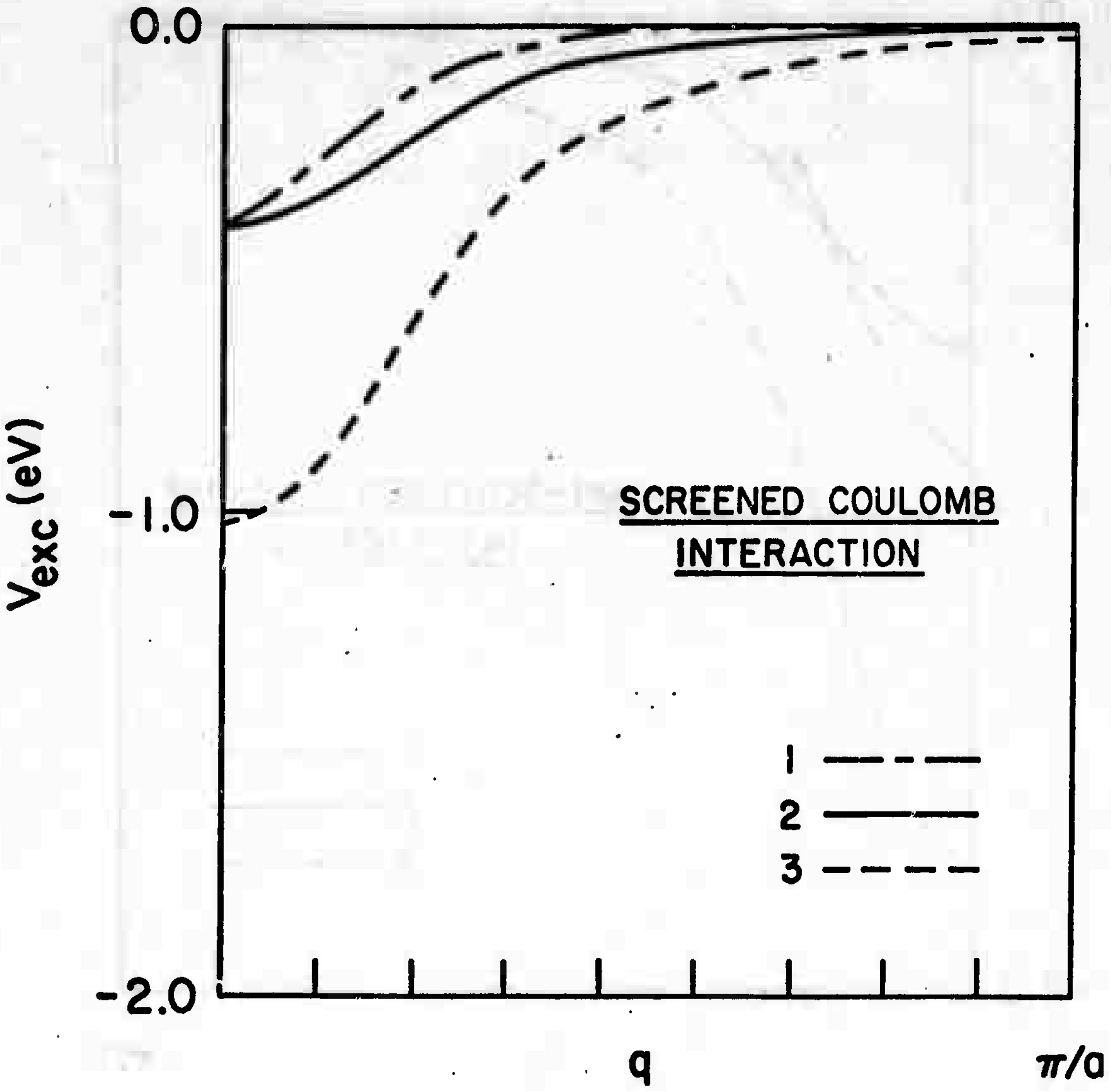


Fig. 2(b) Excitonic interaction as a function of momentum, q, calculated with a screened interaction.

1 - the four-dye glyoxime structure (Fig. I-1, First Annual Technical Report)

2 - the two dye structure of Fig. 1

3 - the four dye structure of Fig. 1.

dye system of Fig. 1, and, in addition, narrows the region in momentum space over which the interaction is effective.

In Fig. 2(b) we show the results obtained when screening is taken in to account. The net effect is that the interaction is weakened appreciably at small momentum transfers but the interaction at larger q remains almost unchanged. Screening also enhances the gain one can get from bringing the polarizable dye into closer proximity to the metal chain as can be seen in comparing 1 and 2 for the screened and the unscreened cases, respectively.

In the above we have used the static screening approximation as derived by Davis using the Thomas-Fermi method. For calculations at finite frequencies the frequency-dependent solution should be used. This is currently being investigated by Bruce Bush.

With the above program for calculating the excitonic interaction resulting from the presence of polarizable molecules it is now possible to calculate the effective interaction for any proposed structure given only the geometry and details of the dye. The next step lies in calculating the transition temperature of the hypothetical structure. To do this we need to have the details of the band structure in the conductive system or the density of states at the Fermi surface, N(0), the Fermi energy and the plasmon energy. Then one needs to solve the integral equation for T_c.

Studies of the band structure of linear chain systems using the Johnson multiple scattering technique are continuing. This has required refinements in the methods for calculating the muffin-tin potential, and the inclusion of programs to utilize the symmetry of the systems in order to reduce the time of computation.

Work has begun on the solution of the equation for the transition temperature. We are following the method of simplifying the integral equation outlined by Kirzhnits et al (Preprint #108, Lebedev Physical Institute, 1970) and Ginzburg (Soviet Physics, Uspekhi 13, 335 (1970)). The combination of this with our results for the effective interaction should enable us to make a reasonable estimate of T_c for compounds for which there is reasonable hope of making. Structurally these would be somewhat similar to the Krogmann salts so that we might expect the properties of the conductive spine also to be similar. With this in mind we have studied the specific heat and magnetic susceptibility of $K_2Pt(CN)_4Cl_{0.3}nH_2O$ in an effort to determine the value of N(0). A somewhat surprising result was obtained.

Specific Heat of One-Dimensional $K_2Pt(CN)_4Cl_{0.3}\cdot nH_2O$

In collaboration with Dr. R. L. Greene of the IBM Research Laboratory, San Jose, we have measured the specific heat of $K_2Pt(CN)_4Cl_{0.3}\cdot nH_2O$ at low temperatures. The details of this are given in the experimental section and have been published (Phys. Rev. Letters 29, 718 (1972)). The results show no linear term in the specific heat and from this one might conclude that N(0)=0. However, we argue on the basis of either the hopping model discussed in the previous report or the interrupted strand model proposed by Kuse and Zeller (Phys. Rev. Letters 27, 1060 (1971)) that at low temperatures the time for thermal equilibrium to be reached in the electron system must be inordinately long. Thus the system remains out of equilibrium and no linear term would be observed in the specific heat because of the conditions under which the experiment was done or could be done. This experiment then does not give us a measure of N(0).

An alternative method for obtaining N(0) is to measure the magnetic susceptibility and extract the contribution of the Pauli temperature independent term. Dave Cahen measured this at room temperature and at liquid nitrogen temperatures for $K_2Pt(CN)_4Cl_{0.3}\cdot nH_2O$ and at the latter obtained a value of 35 ± 5 x 10^{-6} cgs/mole, which yields through the expression $X = \mu^2N(0)$, a value of N(0) of 3.9 ± 1.6 x 10^{21} states/eV-cm^3.

This value of the susceptibility is probably not a reliable measure of N(0) in view of possible contributions from broken chains with odd numbers of electrons which would give a Curie-Weiss contribution instead of a Pauli ter, and, the uncertainty in the time for equilibrium to be reached at lower temperatures. The possibility of a frozen-in Pauli paramagnetism is being studied as is the dependence of the residual susceptibility on structural perfection.

Present Situation

From the rough estimate of N(0) given by the magnetic susceptibility and, the calculation of the excitonic interaction one might expect a reasonably strong coupling constant in the expression for T_c for compounds involving a linear chain of transition metal atoms and a dye array such as that discussed above. However, the problem of synthesizing such a material remains formidable. As discussed in the report by Mayer and Winkler the addition of the side chains to the metal complex can be expected to disrupt the weak forces which hold the metal atoms together and, indeed, this is found in all cases considered to date. One cannot rely on the weak crystalline forces to drive the system to form a stacked array but some form of deliberate control of the structure is necessary. One possibility is to use true covalently-bound metal chains such as those currently under study by Collman and Murphy. The chemistry needed for this is new but progress is being made. Alternately, it may be possible to design structures which through the appropriate location of bonding or blocking groups could be designed to favor a stacked configuration. Modeling studies on these systems are under study.

III. SYNTHETIC PROGRAM

Summary: Our synthetic program is continuing along the lines developed in our previous semi-annual reports. First we have attempted, so far unsuccessfully, to introduce highly polarizeable organic groups (dyes) into complexes which form metal chains in the crystalline state. Second, we have continued efforts to prepare linear polymers with covalently bonded metallic backbones.

The reports of Winkler, Mayer, MacLaury, and Libit describe efforts directed towards the first objective. Dye groups have been introduced into square planar metal complexes but the bulk and strong dipoles of these groups overcome the weak van der Waals forces which usually control intermetallic stacking in the case of simple planar d^8 complex with the result that the stacking interaction and associated electrical conductivity are lost. The concept of forming complexes from dye bases is important and attempts will be made to extend this.

The formation of covalent intermetallic polymers is still frustrated by the lack of a facile, selective metal-metal bond forming reaction. The results of Hoyano, who is studying model reactions, and Murphy, who is making metal-metal bonds using the novel Rh(I) DOH ligand, are promising. New chemistry continues to flow from their work. Stark has not been able to extend the scope of a new metal-metal bond forming reaction discovered by Murphy.

Dye Substituted d^8-Metal Complexes

T. Winkler and C. Mayer

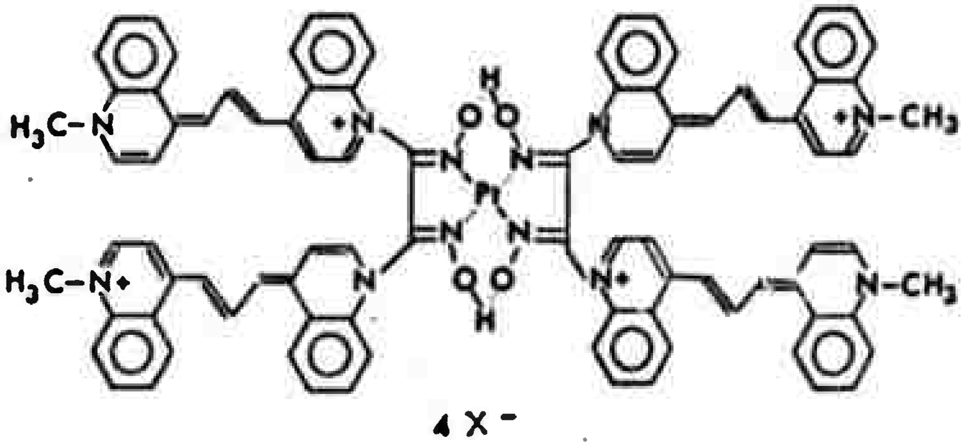
I. Introduction

This report, part three, reviews the continuation of the synthetic 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] (part one) and to ARPA in the First Annual Report[3] (part two).

Section II of this report deals with the preparation of the cyanine dye (diazapolymethinium dye) substituted glyoxime ligand, the synthesis of which has been outlined in report two. Section III gives the design and synthesis of a series of novel iridium and platinum complexes with diazapolymethin dye ligands. Section IV covers the experimental details.

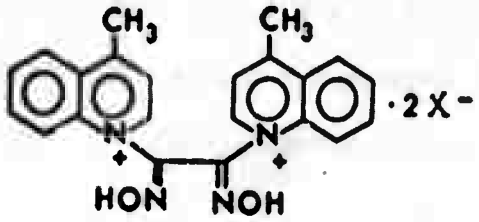
II. Synthesis of the Dye Substituted Dioxime System

In the previous report (part two) the following compound was suggested as a model for a high temperature superconductor.



Ia

The general pathway of the synthesis was outlined there. Details on the formation of II are to be found there also.



II

In the period covering this report we were successful in preparing the entire ligand I of Ia. Yet, there exist considerable difficulties to obtain the compound analytically pure, a necessity for complexation.

II was reacted with 4-β-acetanilinovinyl-quinolinium-methiodide IIIa in lepidine at 120° to give I.

Description of I

The compound is a blue black powder, mp 296° (dec.), highly insoluble in most organic solvents, except methanol and ethanol, in which it is slightly soluble, and soluble in dimethylsufoxide. Analysis of the substance washed in boiling methanol for one day gives correct values. The IR-spectrum in KBr shows primarily the features of the related cryptocyanine with some slight shifts and a few new bands in the fingerprint region. The electronic spectrum in EtOH/DMSO shows a cyanine dye type absorption at 720nm, but with a considerably broader band than the one of cryptocyanine itself, which absorbs at 710nm under the same conditions. The solubility of I is insufficient even in DMSO to obtain a good NMR spectrum. Nevertheless, the oxime protons could be observed at 13ppm I is strongly absorbed on aluminumoxide, not moving on Alox thin layer plates (with pyridine and methanol as eluents) and only partially desorbed by hot DMSO.

Comments on the reaction II and IIIa → I:

II has to be present as the iodide. If the chloride was used I was yielded as a mixed anion salt with a I^- to Cl^- ratio of about one, but varying slightly from experiment to experiment, thus making the microanalysis difficult to interpret. III has to carry the N-acetyl group. The non-acetylated analog of IIIa gives no dye formation.

The solvent has to be lepidine. If pyridine was used the lepidinium in II was exchanged against pyridinium, thus making dye formation impossible.

Complexation of I to form Ia has not yet been resolved. The main problem in this step is the insolubility of the ligand, thus limiting us to the use of DMSO. But we have found that at least for the complexation of dimethylglyoxime with K_2PtCl_4, DMSO is a very appropriate solvent for both components, giving directly, from the reaction mixture, analytically pure $Pt(DMG)_2$ in nice coppery needles. The X-ray shows identity with samples prepared by standard procedures.

K_2PtCl_4 would be unfavorable as X^- in I is I^-, thus leading to mixed anion complexes. K_2PtI_4 is not known (unstable), leaving only PtI_2.

Mixing of I with PtI_2 in DMSO did not lead to precipitation of a product. Evaporating the solvent gives a black powder. Its IR-spectrum gives no hint of a complex. The values obtained from microanalysis are neither correct for the complex nor the mixture of the starting materials.

III. Iridium and Platinum Complexes with Diazapolymethine Dye Ligands

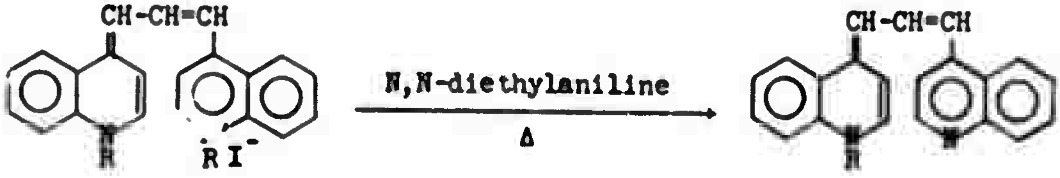
A. Introduction

In this section, we report the synthesis of iridium and platinum complexes with bases, the quaternary salts of which are cyanine dyes.[4] We found, that on complexation, the absorption of the diazapolymethine system shifts up to 100nm to longer wavelengths, thus forming a cyanine-dye-like (diazapolymethinium dye like) system. It did not escape our attention, however, that the cyanine dye base concept has a broad range of application for the realization of a high temperature superconductor. A suitably designed base can be complexed to a variety of materials (e.g. transition metal chalcogenides, glass beads or appropriately substituted, covalently bound metal chains), forming a cyanine dye upon the formation of the complex. Furthermore, it is known, that on alkylation, the corresponding cyanine dyes of the bases are obtained. This reaction allows one to attach the bases to a variety of R-X substances, forming a true cyanine dye as result of the reaction, with the important restriciton, that the R-part does not contain any group that may react with the cyanine base.

B. Bases, the Quaternary salts of which are cyanine dyes

Up to now, we have prepared only cyanine bases with diazanonamethine systems. Shorter chromophores would not fulfill the requirements of the theory and the longer ones are more difficult to handle experimentally. We used two methods of preparation, one patented by Gevaert Photoproducten NV[5], and the other one by Barent and Kendall.[6]

The first method consists of a thermal degradation of a cyanine dye in a high boiling tertiary amine:



IV R = Et
VI R = CH_3

V R = Et
VII R = CH_3

The cyanine dye IV (cryptocyanine) was prepared according to Hamer[7] and degraded to V. Upon recrystallization from acetone, V forms blue-black crystals, mp 161°C. V absorbs at 527nm in EtOH ($\log\varepsilon = 4.48$) and at 499nm in benzene ($\log\varepsilon = 4.57$). Careful addition of HCl-gas produces a cyanine dye with a typical cyanine dye like absorption band at 700nm (EtOH), which is almost indistinguishable from the absorption of cryptocyanine itself (705nm, EtOH). The compound has been claimed but not described by the Gevaert patent. Its structure was confirmed by mass spectrometry. If the reaction is carried out under nitrogen, the yield is improved. A degradation of VI, also prepared according to Hamer, gave either only a very low yield of VII, together with much starting material or a brown degradation product, if the reaction was allowed to continue overnight. A testtube experiment showed that IV can easily be degraded to V by aqueous KOH, whereas with VI, no base is formed. This can be explained with a Hoffmann type degradation as the mechanism of this reaction.

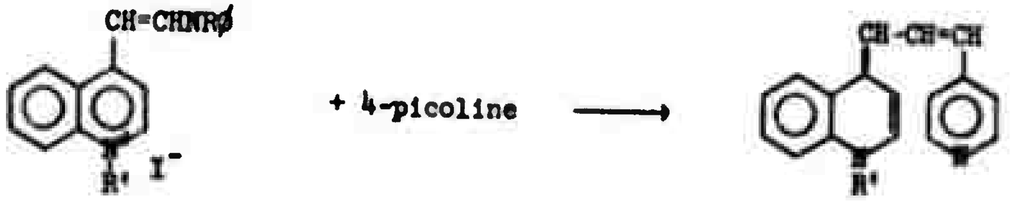
With the aim to reduce the steric hindrance at the complexing site (see part IIID), an attempt has been made to prepare IX by the Gevaert method. Starting material VIII was synthesized according to Rosenhauer and Barlet.[8]

VIII IX

Heating in either N,N-diethylaniline or in N,N-dimethylaniline (for a slightly lower reaction temperature) yielded only a black tar. Therefore, VIII was dissolved in dry pyridine and heated in the presence of KOH for 1 1/2 hour.

The benzene extract contained only a trace of cyanine base (as judged from TLC and UV spectroscopy).

The other method, patented by Barent and Kendall,[6] was therefore used to obtain a base with a pyridine ring as the complexing site. By this method, a cyanine dye base is obtained by heating in the presence of an acid-binding agent, a quinoline base having a reactive methyl group in α or γ-position to the N atom with an alkyl quaternary salt of a heterocyclic N compound having a thioether, selenoether, aminovinyl or substituted aminovinyl group in α or γ-position to the N atom. Apparently, the method seemed to be restricted to quinoline and substituted quinoline bases with methyl groups in α or γ-position (see also ref. 9). Despite this restriction, the following reactions were successful out of a number of other experiments:

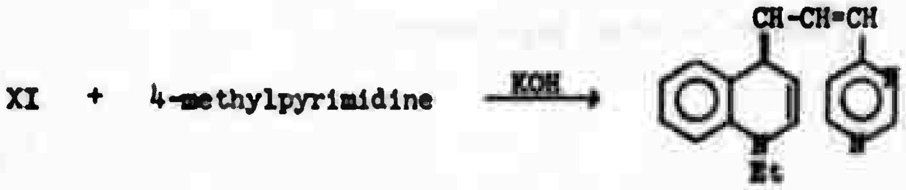


III R = H R' = CH_3
IIIa R = Ac R' = CH_3
XI R = H R' = Et

X R' = CH_3

In this reaction, 4-picoline itself is the acid-binding substance. However, even with the rather reactive 4-(β-acetanilidovinyl)-quinolinium methiodide IIIa, only a very low yield of X is obtained, which can be isolated by chromatography on alumina with benzene/pyridine 5/1. In contrast to this result, the use of a large excess of solid KOH as acid-binding substance gave an almost quantitative yield of X (or 80% after recrystallization), even if the less reactive quaternary salt III is used. X forms red crystals (mp 143°C). λ_{max} in EtOH is 486nm ($\log \varepsilon = 4.39$) and 480 in benzene, whereas the hydrochloride absorbs at 640nm in EtOH. Correct mass spectra for both batches of X have been obtained.

With the aim to obtain a cyanine base, which absorbs at longer wavelengths and fulfills therefore the theoretical requirements better, a cyanine base with a pyrimidine nucleus (XII) has been prepared by the KOH procedure, starting with the ethyl analogue of III, XI:



XII

Unfortunately, a brown side product starts to form prior to the consumption of all starting material. Therefore, the cyanine base XII has to be purified by chromatography on alumina with benzene/pyridine 5/1. Recrystallization from benzene/hexane gives red needles with blue reflection, mp 112°-114°C. XII gives a correct mass spectrum and absorbs at 531nm in EtOH ($\log \varepsilon = 4.64$) and at 506nm in benzene (log 4.57). The hydrochloride absorbs only at 650nm (EtOH).

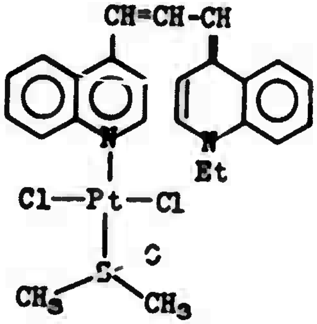
C. Platinum Complexes

The first complexation reactions with V were tried with trans-[Pt(pyridine)$_2$Cl$_2$] (XIII), which was prepared according to ref. 10, in analogy to the following reaction:[11]

$$\text{trans-[Pt(pyridine)}_2\text{Cl}_2] + 2\ \text{quinoline} \longrightarrow \text{trans-[Pt(pyridine)}_2\text{(quinoline)}_2]\text{Cl}_2$$

However, no reaction occurred between V and XIII in a variety of solvents and conditions. No reaction occurred also with trans-[Pt(NH$_3$)$_2$Cl$_2$] (prepared according to ref. 12) and with cis-[Pt(pyridine)$_2$Cl$_2$]. With [PtCl$_2$(DMSO)$_2$], prepared according to ref. 13, the reaction with V proceeds with quantitative yield, as shown in the following equation:

$$\text{V} + [\text{PtCl}_2(\text{DMSO})_2] \longrightarrow$$



XIV

During the reaction, the color of the solution changes from red to deep blue. XIV forms violet crystals with golden luster, and absorbs in EtOH at 605nm and in benzene at 578nm, i.e. upon complexation a shift of 80nm occurs. The NMR spectrum in DMSO-d$_6$ is consistent with the above structure XIV. XIV can also be obtained by the following reaction as judged by comparison of the IR spectra ($CHCl_3$) of the products of both reactions.

$$\underset{XV}{V + K[Pt\,Cl_3\,DMSO]} \xrightarrow{EtOH\ /\ H_2O} XIV + KCl$$

Ref. 13 has been used to prepare XV. The reaction is known for a large number of amines.[14] These complexes are known to have trans arrangement. On the basis of the marked trans effect of DMSO[14,15] and the analogy with the reactions of the other amines,[14] XIV is given the trans structure. The conductivity of a pressed pellet of XIV is smaller than $10^{-13}\,\Omega^{-1}\,cm^{-1}$. The bulky quinoline nucleus and the DMSO ligand probably prevent the metal chain formation.

Reactions between $[PtCl_2(DMSO)_2]$ and X and XII respectively were carried out on a very small scale. The complex of X absorbs at 545nm in EtOH, whereas that of XII shows two peaks, one at 580nm and the other one at 620nm (in EtOH). (This is discussed for compound XXII, which was isolated and characterized.)

Since the very low conductivity of XIV suggests that there is no metal chain in the crystalline state, a series of experiments was undertaken to obtain materials similar to "Krogmann's Salts."[16] Mixtures of solutions of XIV (6 parts) and Pt (IV) compounds (1 part) gave only decomposition of the cyanine base complex. Another pathway, which was tried was the attempted preparation of mixed crystals (1:1) of Pt (II) and Pt (IV) complexes, whereby the Pt (II) part was XIV. It is known that compounds with -Pt(IV)-Cl-Pt(II)-Cl-Pt(IV)- chains are semiconductors.[17]

trans-$[Pt(NH_3)_2Cl_4]$, prepared according to ref. 18, $PtCl_4$ and $(NH_4)_2PtCl_6$ have been reacted with XIV, but without positive result so far. For the same reason, $CuBr_2$ and $CuBr_2.2DMSO$ (prepared according to ref. 19) have been reacted with V under exclusion of H_2O. These reactions lead to the destruction of the diazapolymethine system.

K[Pt Cl_3 pyridine] has been prepared according to Gel'man[20] and reacted with V to give trans-[$PtCl_2$ pyridine (cyanine base V)]. A black powder formed during the reaction. It shows an absorption maximum at 600nm in EtOH. The microanalysis, however, indicates that the material contains cis-[$Pt(pyridine)_2Cl_2$] as side product. Recrystallizations were unsuccessful so far.

D. Complexes with Ir(I)

It is known that $Ir(CO)_{2.9}Cl_{1.1}$ forms coordination complexes of the type $Ir(CO)_2LCl$ with electron donors, e.g. L = amines.[21] The complex with L = p-toluidine forms coppery dichroic needles, with a conductivity around $3 \times 10^{-6} ohm^{-1} cm^{-1}$ (single crystal, two probe) indicating that the metal-metal stacking is retained. This result is strengthened by preliminary x-ray measurements which give a linear arrangement of the Ir with a distance of about 3.38Å.

We coordinated the following bases: pyridine, 4-picoline, 4-phenylpyridine, as well as the dye bases V, X and XII by refluxing a suspension of "$Ir(CO)_3Cl$" in a benzene solution of the calculated (1:1 molar ratio) amount of the appropriate base for about one hour. In the course of the reaction the Ir-carbonyl-chloride dissolved. With the simple heterocycles the solutions turned to a light yellow, with the dye bases a strong bathochromic shift of the starting colors occurred (see below). All complexes were obtained in crystalline form, their size, shape and appearance strongly dependent of the base.

Pyridine complex (XVI): dark needles with green metallic reflection, strong dichroism, transmitted light polarized along the crystal axis red, perpendicular colorless. The complex contains a metal chain, with an Ir separation of 3.62Å, but the Ir atoms are arranged in a zig zag chain (x-ray diffraction analysis by Dr. E. Fleischer).

4-Picoline complex (XVII): brick red needles, no metallic appearance, weak dichroism (red-colorless) as in XVI.

4-Phenylpyridine complex (XVIII): two forms; black needles, strong dichroism (red-yellow) of the type in XVI; yellow orange needles, no metallic appearance, no dichroism. The black needles convert into the yellow orange ones on standing at room temperature. Resublimation of the yellow form produces a mixture of the two forms.

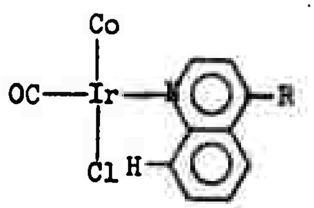
Lepidine complex (XIX): bright yellow fine needles, no dichroism.

Complex with dye base V (XX): hair like needles, steel blue reflection, probably no dichroism, or if very weak (orange-black) with its direction perpendicular to the above mentioned cases and the "Krogmann's Salts,"[16] probably due to the dye system (as is also the reflection).

Complex with dye base X (XXI): fine needles with steel blue reflection, dichroism (red-dark) perpendicular to the one observed in the "Krogmann's Salts."[16]

Complex with dye base XII (XXII): blue black needles, blue reflection, same dichroism as in XXI.

On complexation all the dye systems undergo strong bathochromic shifts, between 60-120nm. The same but even more pronounced effect occurred on quarternization of the dye bases. (Yet, there are systems known which exhibit a hypsochromic shift on quarternization, but those contain other heterocyclic systems than ours do.[22]) So, it seems to be justified to say that on the above complexations a cyanine dye like system is formed by transferring charge from the base onto the metal, despite the fact that the absorption is broader. The complexes XX and XXI give one broad band at 583 (log ε = 4.64) and 542 (log ε = 4.58) respectively (in benzene), whereas complex XXII has about the same bandwidth and intensity but with a splitting at 576 (4.75) and 617nm (4.75, benzene). The reason for the splitting has not yet been established. There could be two reasons for it. One reason could be due to the presence of a second nitrogen in the complexing heterocycle. A splitting of the same kind is observed in 1,1'-dimethyl-4,4'-diphenyl-quinazolino-2,2'-carbocyanine.[4] Second, we might deal with a mixture of two complexes, one with a link at nitrogen one, the other with a link at nitrogen three. The conductivities of pressed pellet samples of the dye complexes are all very small: XX gives less than $10^{-14}\,\mathrm{ohm}^{-1}\mathrm{cm}^{-1}$, XXI shows $4.3 \times 10^{-12}\,\mathrm{ohm}^{-1}\mathrm{cm}^{-1}$ and XXII shows $1.5 \times 10^{-13}\,\mathrm{ohm}^{-1}\mathrm{cm}^{-1}$. The particularly small value of XX in connection with the optical appearance of the lepidine complex XIX strongly suggests the absence of any metal-metal interaction. Models of XIX (and thus also of XX) clearly indicate the impossibility for complexed quinolines to lie flat in the coordination plane due to strong interaction between the "simple" ligands CO or Cl on the metal and the proton at position 8 of the heterocycle.



Hence, the heterocycle is forced to twist around the Ir-N bond, inhibiting interaction of the adjacent Ir, even if there was a columnar packing of the units in the crystal (see below). The way out of this problem appeared to be the complexation of the dye bases X and XII, justified by the x-ray data obtained for the pyridine complex. The corresponding complexes XXI and XXII show a dichroism, though extinction occurs with light polarized perpendicular to the needle axis. Transmitted light polarized along the axis is red in both cases as it is in the pyridine and 4-picoline complexes XVI and XVII respectively. In the dye complexes the polarization effect due to metal-metal interaction (if present) could be obscured by the dye ligand. Needles of cryptocyanine also show dichroism but of perpendicular direction compared to the one observed in the "Krogmann's Salts."

The complexes have a cis arrangement of the ligands, as shown by the following arguments. The IR spectra of all complexes exhibit two carbonyl bands, a narrow one at 2060cm^{-1} and a broader one at 1980cm^{-1} (in KBr). The same appearance and splitting was reported by M. Angoletta[21] for the p-toluidine complex. Since the analysis of the crystal structure of $IrCl(CO)_2$ pyridine shows that the ligands are in a cis arrangement in this complex and since a much smaller difference in frequency would be expected for a trans arrangement[21], the agreement of the IR spectra proves a cis arrangement for all complexes.

As it is supposed that metal-metal stacking in square planar d^8 metal complexes is not a unique and necessary behavior of these systems and as the low electrical conductivities of our dye complexes suggest no or only weak metal interaction, we have undertaken a series of attempts to partially oxidize the metal to eventually induce metal "polymerization," (c.f. "Krogmann's Salts"). But all the oxidizing agents used to date reacted with and affected or destroyed the dye ligand.

Another reason why the system might crystallize with other than columnar packing might be the high asymmetry of the single units, which would lead to an energetically very unfavorable packing with a lot of empty space.

IV. Experimental Section

General Remarks

This section gives only data for completed results. Experiments still in progress are not described. All melting points are uncorrected.

Dilepidiniumdioxime-iodide (II) - CWM40

The same method of preparation was used as described in ref. 2, but the starting material was diiododioxime in this case, formed after a procedure by W. Steinkopf and B. Juergens.[23] The dilepidinium-iodide is much less stable than the chloride analogue. It decomposes within hours and has to be used immediately after preparation. mp ~ 100° (dec.)

4-β-anilinovinyl-quinolinium-methiodide (III) - CWM30

III was prepared according to the orthoformate-aniline method.[4] The 1,1'-dimethyl-4,4'-carbocyanine iodide which was also formed during the reaction could not be completely removed by recrystallization from ethanol as claimed in the literature. Treatment of a boiling ethanol solution with charcoal gave very pure samples of III. It forms dark shiny crystals from ethanol. mp ~ 252° (dec.)

Analysis: $C_{18}H_{17}N_2I$ (MW 388.25)

Calc.	%C 55.58	%H 4.41	%N 7.21	%I 32.68
found	%C 55.48	%H 4.44	%N 7.28	%I 32.42

4-β-acetanilidovinyl-quinolinium-methiodide (IIIa) - CWM30Ac

776 mg of III were suspended in 25 ml acetic anhydride and refluxed until no educt was recognizable in the visible spectrum (after ca. 1 hour). The reaction solution was cooled down to -20°, the black green precipitate filtered off and washed with ether. On drying in high vacuum the compound changed color to a greenish yellow. mp 235° (dec.) Yield 740 mg.

The di-dye substituted dioxime system (I) - CWM33/5

62 mg freshly prepared dilepidiniumdioxide-iodide II and 86 mg of compound IIIa were heated to 100° for 20 minutes in 10 ml lepidine. After cooling 15 ml of ethanol were added and the mixture allowed to stand at -20° for one day, during which a fine black precipitate was formed. This product was filtered through a fine glass sinter filter and extracted with boiling methanol for one day. mp 296° (dec.)

Analysis: $C_{46}H_{38}N_6O_2I_2$ (MW 960.65)

Calc. %C 57.51 %H 3.98 %N 8.75 %I 26.42

found %C 57.25 %H 4.03 %N 8.95 %I 26.7

Trimethin[4-quinoline][4-(1-ethyl dihydroquinoline)] (V) - TW22

The nomenclature of F. M. Hamer is used for the cyanine bases.[9] 3.5g cryptocyanine[7] were mixed with 500ml N,N-diethyl-aniline. The mixture was stirred and refluxed for 2 1/4 hours, protected from light. During this time, nitrogen was bubbled through the solution, and 300ml of the N,N-diethyl-aniline were distilled off. The other 200ml of solvent were removed by steam distillation. The residue was extracted with benzene. Recrystallization from a few ml acetone yielded 1.25g (51%) blue-black crystals, mp 161°.

Analysis: $C_{23}H_{20}N_2$ (MW 324.42)

Calc. %C 85.15 %H 6.21 %N 8.64

Found %C 84.93 %H 6.20 %N 8.59

λ_{max} 499nm (log ε = 4.57, benzene), 527nm (log ε = 4.48, ethanol), 509nm (log ε = 4.62, acetone)

MS: 324 (100%, M^+), 295 (11%, $M-C_2H_5$), 293 (12%), 196 (24%, $M-C_9H_6N$), 184 (15%), 167 (10%, $M-C_{11}H_{11}N$), 148 (11%), 143 (11%)

Trimethin[4-pyridine][4-(1-methyldihydroquinoline)] (X) - TWM48,TW40

150mg 4-(β-anilinovinyl)-quinolinium methiodide,[4] 15ml dry 4-picoline and 300mg KOH were refluxed for 2 1/2 hours. The solution was diluted with benzene and extracted with water until the water layer was colorless. The benzene solution was dried over Na_2SO_4 and the solvents were removed under vacuum. Recrystallization from benzene/hexane furnished 85mg (85%) red needles, mp 143°.

Analysis: $C_{18}H_{16}N_2$ (MW 260.34)

Calc. %C 83.04 %H 6.19 %N 10.76

Found %C 82.27 %H 6.25 %N 10.68

λ_{max} 480nm (benzene), 486nm (log = 4.39, ethanol)

MS: 261 (19%), 260 (100%, M^+), 259 (72%), 258 (12%), 244 (10%), 243 (8%), 182 (23%, $M-C_5H_4N$), 181 (10%)

Trimethin[4-pyrimidine][4-(1-ethyldihydroquinoline)] (XII) - TW52

503mg 4-(β-anilinovinyl)quinolinium-ethiodide,[4] 3.7g 4-methyl-pyrimidine (ROC/RIC) and 3g KOH were heated at a bath temperature of 135°C for 70 min. The resulting mixture was extracted with methanol. The solution was diluted with benzene and extracted with water. The aqueous extracts were dark brown. The benzene solution was dried over Na_2SO_4 and the solvents removed under vacuum. The substance was chromatographed on alumina with benzene/pyridine 5/1.

Recrystallization from benzene/hexane gave 120mg violet needles, mp 112-114 °C.

Analysis: $C_{18}H_{17}$[illegible], (MW 275.37)

Calc. %C 78.52 %H 6.22 %N 15.26

Found %C 77.19 %H 6.14 %N 15.44

λ_{max} 506nm (log ε = 4.57, benzene), 531nm (log ε = 4.64, ethanol)

MS: 275 (38%, M^+), 196 (26%, $M-C_4H_3N_2$), 195 (100%, $M-C_4H_4N_2$), 167 (10%), 166 (16%), 157 (16%)

[$PtCl_2$ DMSO trimethin[4-quinoline][4-(1-ethyl dihydroquinoline)]] (XIV) - TW27

88mg V and 113mg $PtCl_2(DMSO)_2$ were stirred in 5ml dry DMSO (dimethylsulfoxide) in the dark for 1 hour. The solution was then concentrated to 1 ml at high vacuum and mixed with 50ml hot acetone, which furnished 142mg violet crystals with golden luster. The material looses the luster at 220°C, but does not melt up to 325°C.

TW32

106mg V were dissolved in 200ml 70% EtOH and 130mg $K[PtCl_3DMSO]$ were added. The mixture was stirred for 8 hours at room temperature in the dark and allowed to stand overnight. The violet precipitate formed was filtered, washed and dried. Recrystallization from acetone yielded 160mg violet crystals with golden luster (73%). Absorption spectra in the visible region, IR and microanalysis are identical with those obtained for the product of the first procedure.

λ_{max} 578nm (benzene), 605nm (ethanol), 600nm (log ε = 4.69, acetone)

IR ($CHCl_3$, 1mm, cm^{-1}): 1630, 1385, 1135, 1015, 990, 525, 435

NMR (T-60, DMSO-d_6): 1.28 (T, 3H, methylprotons), 2.50 (S, 6H, methylprotons of the DMSO ligand), 4.08 (0, 2H, metyleneprotons), 6.5 - 9.5 (M, 15H, vinyl and aromatic protons)

Analysis: $C_{25}H_{26}N_2OSCl_2Pt$ (MW 668.56)

Calc.	%C 44.91	%H 3.92	%N 4.19	%O 2.39	%S 4.80	%Cl 10.61	%Pt 29.18
Found	%C 45.04	%H 3.90					
Found	PC 45.13	%H 3.91	%N 4.37		%S 4.98	%Cl 10.68	%Pt 29.03

Iridium-carbonyl-chloride-amine complexes

All the iridium complexes have been prepared by the same method: refluxing a suspension of $Ir(CO)_{2.9}Cl_{1.1}$ in benzene containing an equimolar amount of the appropriate base dissolved in it. Reaction time for 0.4 mMol runs in 50ml dry solvent is ca. 1 1/2 hours. After that the reaction mixture was filtered, evaporated, redissolved in a small amount of benzene and filtered through Pyrex wool into a test tube. The solution then was concentrated in a stream of argon to 1-2 ml, hexane added until the mixture just became cloudy. Cooling to -20° yielded the crystalline products. Yields after recrystallization about 80%.

Pyridine complex (XVI) - CWM42

Dark needles, green metallic reflection. mp 72° (dec.)

Analysis: $C_7H_5NO_2ClIr$ (MW 362.77)

Calc.	%C 23.18	%H 1.39	%N 3.86	%Cl 9.77
Found	%C 23.27	%H 1.53	%N 3.92	%Cl 9.56

4-Picoline complex (XVII) - CWM44

Brick red needles, no metallic reflection, mp 111°. No analysis due to the fact that by recrystallization the colorless byproduct could not be removed. Attempted chromatography of the compound on alox led to its destruction.

4-Phenylpyridine complex (XVIII) - CWM46

On crystallization by the above mentioned method two kinds of crystals are formed: black needles, metallic reflection and an orange yellow form, mp 131°(dec.). The black form converts to the yellow orange one on standing at room temperature. Sublimation of the orange yellow form at 100° (.1mmHg) again produces both appearances.

Lepidine complex (XIX) - CWM43

Bright yellow fine needles, mp 125° (no decomposition).

Analysis: $C_{12}H_9NO_2ClIr$ (MW 426.86)

Calc. %C 33.76 %H 2.12 %N 3.28 %Cl 8.30 %Ir 45.02

Found %C 33.96 %H 2.21 %N 3.33 %Cl 8.46 %Ir 44.64

Complex with dye base V (XX) - CWM37

Dark hairlike needles, steel blue reflection, mp 165° (dec).

Analysis: $C_{25}H_{20}N_2O_2ClIr$ (MW 608.25)

Calc. %C 49.37 %H 3.31 %N 4.61 %Cl 5.83 %Ir 31.59

Found %C 49.55 %H 3.39 %N 4.35 %Cl 5.80 %Ir 31.38

λ_{max} (log ε, benzene) 583nm (4.64)

Complex with dye base X (XXI) - CWM49

Dark hairlike needles, steel blue reflection, mp 170°(dec.).

Analysis: $C_{20}H_{16}N_2O_2ClIr$ (MW 544.01)

Calc. %C 44.15 %H 2.92 %N 5.15 %Cl 6.52 %Ir 35.33

Found %C 44.32 %H 2.99 %N 5.23 %Ir 35.03

λ_{max} (log ε, benzene) 543 (4.58)

Complex with dye base XII (XXII) - TW53

Blue black needles, blue reflection, mp 153° (dec.).

Analysis: $C_{20}H_{17}N_3O_2ClIr$ (MW 559.03)

Calc. %C 42.97 %H 3.07 %N 7.52 %Cl 6.34 %Ir 34.38

Found %C 42.94 %H 3.28 %N 7.34 %Cl 6.70 %Ir 34.8

λ_{max} (log ε, benzene) 576nm (4.75), 617nm (4.75); λ_{min} 596nm (4.70)

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The Synthesis of Stacked Square Planar Iridium Complexes

Michael R. MacLaury

Introduction

Work has continued in an attempt to systematically synthesize square planar iridium(I) complexes that will stack to form columns of iridium atoms in the solid state. The series, $Ir(CO)_2(RCOCHCOR')$, reported upon in the third Semi-Annual Report, has been extended and several other bidentate ligands have successfully been complexed to iridium.

Results and Discussion

A more detailed look at the black material formed from either $[Ir(cyclootadiene)Cl]_2$ or $[Ir(cyclooctene)_2Cl]_2$ and CO confirms that under some conditions it reacts as $Ir(CO)_3Cl$. However, it is not crystalline, as shown by an X-ray powder pattern, and it does not sublime in a stream of CO at 160 - 200°C as $Ir(CO)_3Cl$ does. This black material continues to be a useful starting material for some reactions but its composition is not known. (II-30y, III-9y).[1]

The oxidation of $Ir(CO)_2(RCO)_2CR')$ with CCl_4 where $R = CH_3$, CH_3CH_2, CF_3, $R' = H$ and $R = CH_3$, $R' = CH_3$ has been studied and in the case of $Ir(CO)_2(acac)$ the product was isolated. In the other cases the product was observed by noting the change in the infrared stretching frequency of the Ir-CO band. In all cases the $^{\nu}$Ir-CO were raised

80 - 100 cm^{-1}. Analysis showed that CCl_4 had been oxidatively added to give $Ir(CO)_2(Cl)(CCl_3)(acac)$. This material is only stable a few days in air. (II-65y, II-66y, II-712, III-ly, III-20y).

A number of attempts have been made to prepare some complexes of iridium containing unsaturated tetradentate ligands. Fleischer has reported an Ir(III) complex of hematoporphyrin(IX)diethyl ester[2] but his analytical data is poor and he may not have had pure material. In our hands all the attempts to coordinate (DOH) [bis(diacetylmonoxime-imino)propane 1,3], (salen), (dmg), or (dip) [2,2'-(trimethylene bis-(nitrilomethylidyne))dipyrrole][3] with iridium were unsuccessful. The reaction conditions employed are listed in Table I.

Preliminary X-ray data[4] on $Ir(CO)_2((CH_3CO)_2CCH_3)$ indicate that in the solid state the molecules form dimers. The Ir-Ir separation is 3.29 Å and the dimer units are about 6 Å apart from each other. It is interesting to note that in $Ir(CO)_2((CH_3CO)_2CH)$ the Ir-Ir separation is not much smaller (3.20 Å), indicating that the size of the methyl group does not interfere with close metal packing. But the methyl group is big enough to prevent the close packing of more than two molecular units. It appears that the formation of columnar stacks in single crystals containing neutral d^8 iridium complexes is controlled by subtle interactions of the crystal packing forces rather than iridium-iridium orbital interactions.

A separate section of this report (G. Wrighton and M. R. MacLaury) presents reflectance data for a number of iridium(I) compounds. The

Table I

Attempted Coordination Reactions

			Reference
DOH	$Ir(CO)_3Cl$, $NaHCO_3$, C_6H_6, I_2	uncharacterizable	III-26w
DOH	$\phi_4As[Ir(CO)_2Cl_2]$, $NaHCO_3$, C_6H_6, I_2	"	III-26y
DOH	$IrCl_3 \cdot H_2O$, LiCl, CO, EtOH	"	III-27w
DOH	$IrCl_3 \cdot H_2O$, t-butylalcohol	"	III-29w
DOH	K_2IrCl_6, CO, 2-methoxy ethanol	"	III-30y
DOH	$Ir(CO)_2(Cl)$(p-toluidine), C_6H_6	"	III-53w
DOH	$[Ir(C_8H_{14})_2Cl]_2$, $NaHCO_3$, C_6H_6, I_2	"	III-60y
dmg	$IrCl_6^{-3}$ (from $IrCl_6^{-2}$ + $NaNO_2$)	H_2O soluble	III-27y
dmg	$IrCl_3 \cdot H_2O$, t-butylalcohol	H_2O soluble	III-28y
dip (III-46y)	$IrCl_3 \cdot H_2O$, t-butylalcohol	uncharacterizable	III-47w
dip	$IrCl_3 \cdot H_2O$, LiCl, CO, EtOH	"	III-47y
dip	K_2IrCl_6, CO, 2-methoxyethanol	"	III-48w, y
dip	$Ir(CO)_3Cl$, $NaHCO_3$, C_6H_6	"	III-49w 51y, 52y
dip	$Ir(CO)_2(Cl)$(p-toluidine), C_6H_6	"	III-54w
salen	$Ir(CO)_2(Cl)$(p-toluidine), C_6H_6, I_2	"	III-59y

suggestion is made that reflectance measurements may be a simple technique to ascertain the presence of metal stacks.

The bis(iridium dicarbonyl)tetraketone $[Ir(CO)_2)_2(C_6H_5COCHCO$-$CHCOCHCOC_6H_5))$ was prepared in an attempt to obtain a double stacked compound similar in crystal structure to $Ir(CO)_2(acac)$. Although no crystal structure has been determined the bright red color of the compound suggests that stacking does not take place. One expects a metallic luster to indicate the existence of stacking.

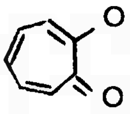
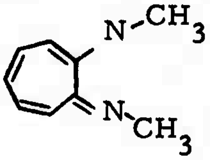
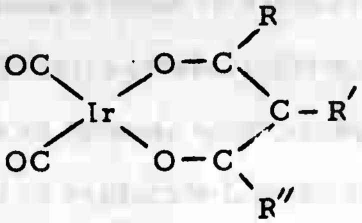
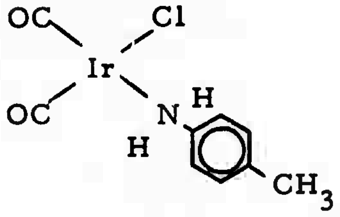
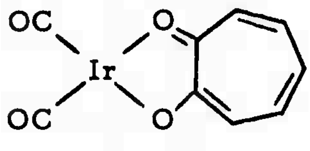
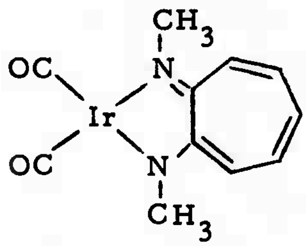
Two other compounds were prepared with the hope that they also would stack, $Ir(CO)_2$ () and $Ir(CO)_2$(). Both of the cycloheptatriene ligands are thin and planar and one might expect this to facilitate stacking. The compounds are both black microcrystalline powders. Attempts to grow crystals large enough for X-ray analysis have not been successful.

Table II

Summary of Compounds Prepared



R	R'	R''	Color
CH_3	H	CH_3	gold-luster
CF_3	H	CF_3	green-luster
CH_3CH_2	H	CH_3CH_2	gold-luster
$CH_3CH_2CH_2$	H	$CH_3CH_2CH_2$	red oil
$(CH_3)_2CHCH_2$	H	$(CH_3)_2CHCH_2$	red
C_6H_5	H	C_6H_5	red
CH_3	H	OCH_2CH_3	gold-luster
CH_3	CH_3	CH_3	orange
CH_3	H	1-azulene	blue
			blue luster
			black
			black luster

Experimental

All reactions were carried out under Ar using solvents dried with 4A mol sieve and degassed with Ar. In most cases the benzene used was distilled from Na/K under N_2. Except where noted, reagents were used directly from the suppliers with no further purification. Infrared spectra were recorded on a Perkin-Elmer Model 457 grating spectrometer. NMR spectra were recorded on a Varian T-60. Microanalyses were performed by the microanalytical laboratory of this department.

1, 1, 1, 5, 5, 5-hexa fluoro-2, 4-pentanedianato dicarbonyl iridium(I), $((F_3CCO)_2CH)Ir(CO)_2$.

$(Ir(C_8H_{14})_2Cl)_2$ (0.78 g, 1.6 x 10^{-3} mol) were dissolved in 300 ml pet ether and CO bubbled thru the solution. The black precipitate was collected and washed with pet ether. 1, 1, 1, 5, 5, 5, Hexafluoro-2, 4-pentanediene (MC/B) (0.44 g, 2.1 x 10^{-3} mol) was added to a benzene (300 ml) suspension of the black precipitate. Excess $NaHCO_3$ was added to neutralize the HCl. The solution was heated at reflux under Ar for 3 hours. The solution was cooled, filtered, the residue was washed with Et_2O, and the solvent removed under reduced pressure (green-lusterous crystals were washed with a small portion of cold hexane (0.45g, 60%). The ir (C_6H_6) shows ν_{Ir-CO} at 2087 and 2015 cm^{-1}. The pmr in C_6D_6 shows only one peak at 6.08 τ. The material sublimes easily and decomposes at $T > 100°C$. (II-69w, III-62 w).

Di-(3-methylbutanoyl)methane dicarbonyl iridium(I) $((CH_3)_2CHCH_2CO)_2CH)$-$Ir(CO)_2$.

$(Ir(COD)Cl)_2$ (0.25g, 7.5 x 10^{-4} mol) excess Na_2CO_3, and 0.19 g (1.0 x 10^{-3} mol) $((CH_3)_2CHCH_2CO)_2CH_2$ from L. Libit were dissolved in 25 ml acetone. The solution was heated at reflux under Ar for 40 min. The solution was then cooled and CO bubbled through the solution. The mixture was filtered and the solvent removed under reduced pressure. The impure product was extracted from the brown oily residue by vacuum sublimation (T = 95°C, $P < 20$ x 10^{-3} torr). Green crystals formed at -78°C but became a red oil at room temperature. At -78°C the crystals were repeatedly washed with cold Et_2O to remove the excess free ligand. When pure, the product formed green-red crystals at room temperature (II-73w).

2,4,6-cycloheptatriene-1,2-dianatodicarbonyl iridium(I): $Ir(CO)_2(C_7H_5O_2)$

$(Ir(COD)Cl)_2$ (0.31g, 9.4 x 10^{-4} mol), excess $NaHCO_3$ and 0.12g (1 x 10^{-3} mol) Tropolone (Aldrich) were dissolved in 50 ml acetone and heated at reflux under Ar for 3 hr. Carbon monoxide was bubbled through the cooled solution. The color was observed to change from cherry red to orange. The solvent was removed under reduced pressure and the bronze-colored solid was transferred to a sublimation apparatus. The product was sublimed (T = 150 P 10 x 10^{-3} torr) and recrystallized from acetone (0.12g 36%). The ir (KBr disc) shows $^{\nu}$Ir-CO at 2060 and 2010 cm^{-1}: mp 210° (dec).

Anal. Calcd for $Ir(C_9H_5C_4)$: C, 29.27; H, 1.36; Ir, 52.04. Found: C, 29.91; H, 1.59; Ir, 51.7. (III-2w, 32y).

1-Azulyl 3-methyl 1,3 butanedianotodicarbonyl iridium(I), $Ir(CO)_2$-($C_{10}H_9COCHCOCH_3$)

$Ir(CO)_3Cl$ (0.35g, 1.1 x 10^{-3} mol), excess $NaHCO_3$, and 0.25g (1.2 x 10^{-3} mol) 1-azulyl 3-methyl 1,3-butanedione from L. Libit were suspended in 120 ml benzene, and heated at reflux under Ar for 3 days. The cooled solution was filtered and the volume reduced under reduced pressure. The product was recrystallized from either acetone or acetonitrile to give tiny blue crystals (0.3g 69%). The ir (KBr disc) showed $^{\nu}$Ir-CO at 2065 and 1983 cm^{-1}. The pmr in C_6D_6 showed peaks at 6.3 (1) $^{\tau}$ and 1.8 (3): mp 170° (dec). Product sublimes without decomposition only in good vacuum ($P < 5 \times 10^{-4}$ torr).

<u>Anal</u>. Calcd for $Ir(C_{16}H_{11}O_4)$: C, 41.82; H, 2.41; Ir, 41.83. Found: C, 42.26; H, 2.66; Ir, 41.2. (III-17w, 21y, 24y, 38y, 42w).

1-7-diphenylheptane-1,3,5,7 -tetraone bis dicarbonyl iridium(I). $[Ir(CO)_2]_2[C_6H_5COCHCOCHCOCHCOC_6H_5]$

1,7-diphenylheptane-1,3,5,7-tetraone was prepared by the method of Hauser[5] and mass spectrum of product confirmed the structure. $Ir(CC)_3Cl$ (0.17g, 5.4 x 10^{-4} mol), excess $NaHCO_3$, and 0.09g (2.8 x 10^{-4} mol) tetraketone were suspended in 40 ml benzene and heated at reflux under Ar for 3 days. The cooled solution was filtered and the volume reduced. Crude crystalline product formed upon cooling. Product was recrystallized from CH_2Cl_2. The ir (KBr disc) showed ν_{Ir-CO} at 2065 and 1990 cm^{-1}.

Anal. Calcd for $Ir_2(C_{23}H_{14}O_8)$: C, 34.41; H, 1.76; Ir, 47.89. Found: C, 34.30; H, 1.95; Ir, 46.0. (III-11y, 13y, 15w, 16w, 25y).

N,N'-dimethylaminotroponeimino dicarbonyl iridium(I), $Ir(CO)_2(C_7H_5(NHCH_3)(NCH_3))$.

$Ir(CO)_3Cl$ (0.36g, 1.2 x 10^{-3} mol), excess $NaHCO_3$, and 0.19 g (1.3 x 10^{-3} mol) N, N'-dimethyl aminotropaneimine (supplied by R. E. Benson of the DuPont Exp. Sta.) were suspended in 80 ml benzene and heated at reflux under Ar for 1 hour. The cooled orange-brown solution was filtered and the residue washed with several portions of benzene. Tlc (1:1 ether/hexane) shows free ligand (remains at origin) and product (moves with solvent front). The solvent was removed and the acetone-soluble portion was passed through a short silica gel column and eluted with 1:1 ether/hexane. The yellow eluted fraction produced small dark crystals. The ir (KBr disc) showed $^{\nu}$Ir-CO at 2003, 1945, and 1915 cm^{-1}. The sample sublimes to a dark mirror. (T ~ 90 - 100°C $P < 10 \times 10^{-3}$ Torr).

Anal. Calcd for $Ir(C_{11}H_{11}N_2O_2)$: C, 33.41; H, 2.80; N, 7.08; Ir, 48.61. Found: C, 33.32; H, 2.82; N, 7.24; Ir, 47.9. (III-44w).

2,4-Pentanedionato dicarbonyl trichloromethylchloride iridium(III) $Ir(CO)_2Cl(CCl_3)(acac)$.

$Ir(CO)_2(acac)$ was dissolved in CCl_4, freshly distilled from P_2O_5 under Ar, to give a bright yellow slightly turbid solution. The CCl_4 was removed under reduced pressure at or below room temperature. The yellow oily solid was extracted with several portions of hot hexane. Upon cooling of the hexane solution cream colored crystals formed. These crystals are stable in air for several days, after which they decompose to a dark oil with the odor of HCl. The ir (C_6H_6) shows: ν_{Ir-CO} at 2150, 2105, and 2080 (weak) cm^{-1} and in KBr ν_{Ir-CO} at 2155, 2110, 2075 (weak) cm^{-1}. The rest of the ir spectrum is similiar to $Ir(CO)_2$ (acac) except for strong bands at 737, 725 and 300 cm^{-1}. The first two bands can be assigned to ν_{C-Cl_3} and the third band can be assigned to ν_{Ir-Cl}. The nmr in C_6D_6 of a 1 : 1 mixture of $Ir(CO)_2$ (acac) and $Ir(CO)_2(CL)(CCl_3)$(acac) clearly shows two CH_3 peaks and a doublet for the methine proton at δ 1.55 and 1.60 and 5.15 respectively.

The Raman spectrum shows a number of low energy peaks with only three corresponding to ir bands (300, 725, and 735 cm^{-1}) and no bands higher than 735 cm^{-1}.

Anal. Calcd for $Ir(C_8H_7O_4Cl_4)$: C, 19.17; H, 1.41; Cl, 28.30; Ir, 38.35. Found: C, 19.15; H, 1.54; Cl, 27.47; Ir, 38.8. (III-20y, III-24w).

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(1) These numbers refer to laboratory notebook and page.

(2) N. Sadsivan, E. B. Fleischer, J. Inorg. Nucl. Chem., **30**, 59 (1968).

(3) J. H. Weber, Inorg. Chem., **6**, 258 (1967).

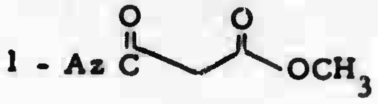
(4) E. B. Fleischer, Contract Monitor's Seminar, 10 August 1972.

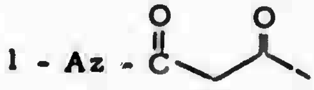
(5) K. G. Hampton, T. M. Harris, C. M. Harris, C. R. Hauser, J. Org. Chem., **30**, 4263 (1965).

RESEARCH REPORT

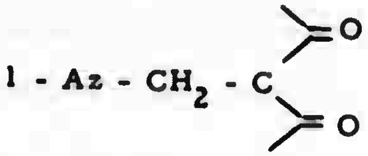
Lawrence Libit

Compound List--Superconductors

(1)  Tl complex (1a)

(2)  Ir complex (2a)

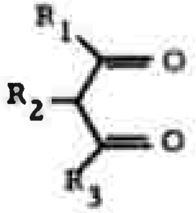
(3) 

(4) 

Superconductors*

Introduction

In the last report[1] we described our attempts to prepare an acetylacetone derivative with R_1, R_2 or R_3 replaced by an organic dye. Our first choice of a dye was the azulene nucleus itself. We



chose azulene for the dye because it is a neutral molecule and because it contains an optical transition that can be shifted and intensified by the proper choice of substituents. We intended to form the iridium dicarbonyl acetylacetonate derivative of such a dye containing ligand in the hope that we would obtain the usual $Ir(CO)_2AcAc$ crystal packing pattern in which the iridium atoms are arranged in a series of chains (the internuclear distance in a given chain is 3.20 Å). If such a crystal pattern could be obtained, the dye might exitonically couple with the electron in the metallic spine and unusual (e.g. super) conduction properties along the c axis of the crystal might be observed.

The present report describes the successful synthesis of two azulene containing β-dicarbonyl compounds 1 and 2. For a description of the iridium complexes of these ligands see the research report of M. MacLaury.

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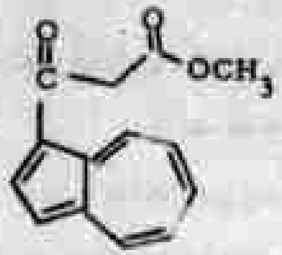
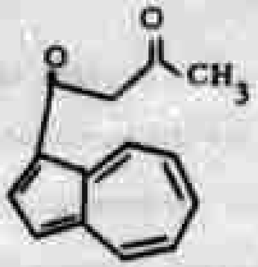
* The following two papers are the result of a collaborative effort by M. MacLaury and L. Libit.



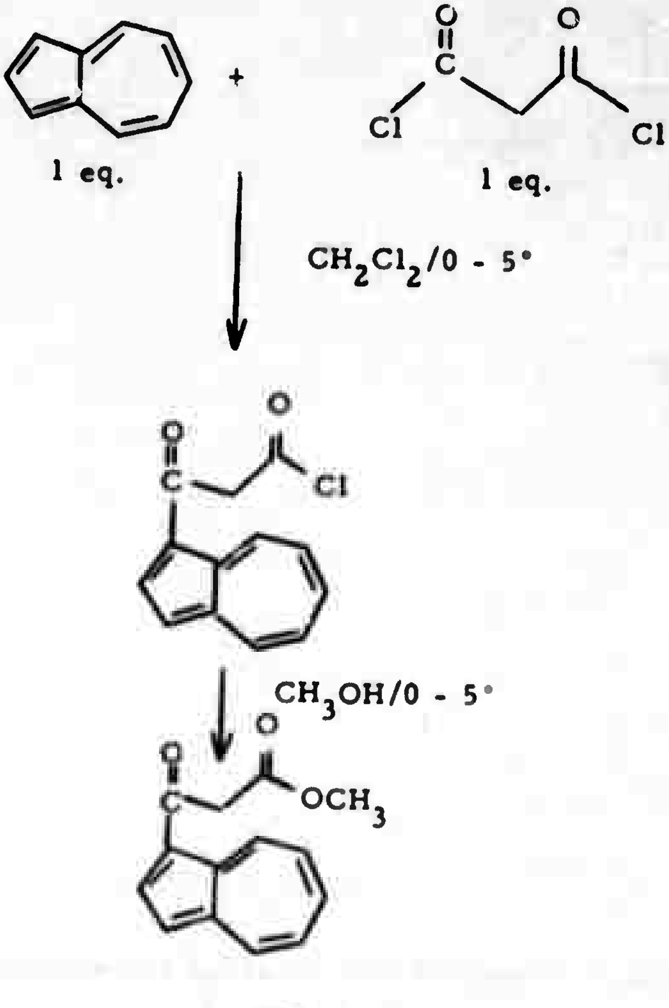
1



2

Part A. The Synthesis of 1

An exhaustive search of the literature revealed a method for the preparation of 1.[2] Since very little experimental detail was contained

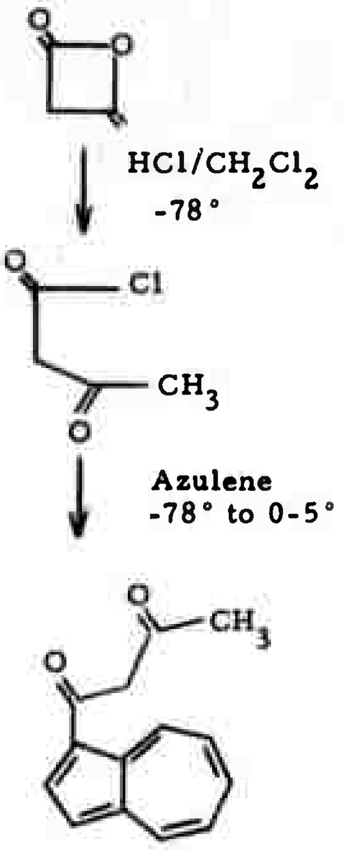


1, 50% yield

in the literature citation, several reaction conditions were employed. The best procedure for the production of 1 is described in the experimental section. Several attempts were made to prepare a bis azulene adduct (di(1-azulenoyl)methane) of malonyl dichloride but in each case only 1 was formed following a methanolic work up [azulene/dichloride:: 2 : 1].

Part B. The Synthesis of 2.

The synthesis of the title compound is outlined below:



2, 28%

In this reaction no consumption of azulene was observed below -20°.

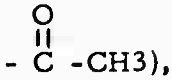
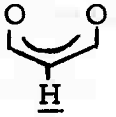
The Preparation of a Methyl 1-(1-Azulenoyl)Acetate (1)[2]

To a solution of azulene (128 mg., 1.0 mmole) and dichloromethane (5 ml.) at 0 - 5° under nitrogen was added malonyl dichloride (48.5 μl, 0.5 mmole). After 30 min. at 0 - 5° methanol (2 ml) was added and the mixture was stirred 10 min. at room temperature. At this time ether (20 ml) and water (20 ml) were added. The separated ether phase was dried ($MgSO_4$), filtered and concentrated to produce a residual oil (11 mg). The crude product was purified by PLC (2 : 1 :: ether : hexane) followed by crystallization from a small amount of ether. Purified yield: 50 mg, 0.22 mmole, m.p. 67 - 70°; Lit[2] m.p. 70°. No evidence for di(1-azulenoyl)methane was obtained. The use of stoichiometric amounts of malonyl dichloride and azulene gave a 50% yield of purified PLC: 5 : 3 :: ether : hexane.

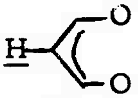
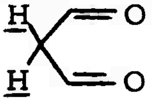
The nmr spectrum ($CDCl_3$) displayed signals at 3.8 (singlet, 3H, OCH_3), 4.2 (singlet, 2H, $\overset{O}{\overset{\|}{C}} - CH_2 - \overset{O}{\overset{\|}{C}}$) 7.2 - 8.5 (multiplet, 6H, azulenyl ring protons) and 9.7 (doublet, 1H, J = 4 cps $C_8 - \underline{H}$ azulenyl proton) ppm. The UV spectrum (ether) displayed maxima at 540 (E = 570), 465 (E = 660), 390 (E = 8,5000) and 310 (E = 3.58×10^4) NM. The spectrum was consistent with that reported previously.[2] The mass spectrum displayed a molecular ion at 228 M/e.

The Preparation of 1-Azulenoylacetone (2)

Freshly distilled diketone (238 mg, 2.8 mmole) was dissolved in methylenechloride (20 ml) and the solution was cooled to -78°. Dry HCl gas was bubbled thru this mixture at -78 for 1 min. to produce acetoacetylchloride.[3] At this time a vacuum was applied (20 mm) to the system for 5 min at -78°. Then azulene (360 mg, 2.8 mmole), in a few milliliters of dichloromethene, was added and the mixture was stirred 1 hr at 0 - 5°. The solvent was removed at reduced pressure and the title compound was isolated by chromatography on silica gel (2 : 1 hexane : ether) in 28% yield.

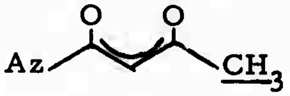
The nmr spectrum (CCl_4) displayed signals at 2.0 (singlet, 3H,  $-\overset{O}{\overset{\|}{C}}-CH3$), 6.0 (singlet  , 1 H), 7.2 - 8.6 (multiplet, azulenyl ring protons, 6 H) and 10.0 (doublet, J = 10 cps, C_8 - H, 1 H) ppm. The mass spectrum displayed a molecular ion at 212 m/e.

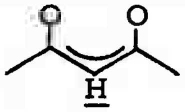
The Thallium Complex of 1-Azulylacetoacetate (1)

To Thallous ethoxide (126 mg, 0.5 mmole) was added a solution of the β-ketoester (114 mg, 0.5 mmole) in benzene (3 ml). After 2 hr, the solvent was removed at reduced pressure and the residue dissolved in hexadeuterobenzene. The nmr spectrum of this material displayed characteristic resonances at 3.6 (singlet, 3 H, complexed OCH_3), 6.0 (singlet, 1 H, complexed ) and an azulenic aromatic multiplet (no area could be recorded due to the interference of the benzene signal). Significantly the  chromophere was absent in this spectrum; thus, starting material was entirely consumed in this reaction. No attempt was made to purify this material as it was obtained as an oil and it was to be used as an intermediate in the preparation of the iridium dicarbonyl complex of the ligand.

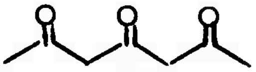
The Iridium Complex of 1-Azulenoylacetone (2)

A solution of 1-azulenoylacetone (2) (170 mg, 0.8 mmole) thallous ethoxide (200 mg, 0.8 mmole) and benzene (25 ml) was stirred under argon 5 hr. Then μ μ'-dichlorotetrakis (cyclooctene)diiridium(I) was added. The solution was filtered and carbon monoxide was bubbled through the filtrate. The mixture was concentrated and crystals (110 mg) were obtained from a small amount of benzene and hexane.

The nmr spectrum (deuterobenzene) displayed characteristic signals at 1.8 (singlet, 3H, complexed 

) and 6.1 (singlet, 1 H, complexed 

) ppm. The remainder of the spectrum displayed the characteristic azulenic chromophores but the area could not be recorded due to the interference of the benzene signal. The ir spectrum (KBr) displayed characteristic bands at 1980 and 2350 (cis CO stretches in complex) cm^{-1} and 1525 (complexed β-diketone moiety) cm^{-1}. The spectra are essentially identical to the iridium dicarbonyl complex obtained from the direct reaction of the ligand with iridium tricarbonyl chloride. A correct elemental analysis was obtained from the latter material whereas the material described herein failed to give a correct analysis.

The Preparation of  (3)

Diketene (1g, 11.9 mmole) was added in 150 μl portions to a mixture of water (108 mg, 6 mmole) and DABCO (10 mg) at 0 - 5°. After

5 hr, ether (50 ml) was added and the solution was dried over sodium sulfate, filtered and concentrated to a residual oil. The crude product was taken up in methanol (2 ml). To this mixture was added a hot solution of copper acetate monohydrate (1.2 g) and water (20 ml). A complex formed immediately and was isolated by centrifugation. The powder thus obtained was dissolved in 10% sulfuric acid and the pure triketone (300 mg, low melting solid) was isolated by extraction with ether. The nmr spectrum (CCl_4) was identical with that reported previously.[4]

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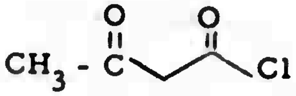
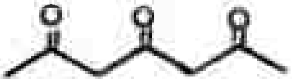
(1) Lawrence Libit, "New Superconductors", Third Annual Technical Report, 8/1/71 to 1/31/72, ARPA Order No. 1681.

(2) 

W. Treibs, Naturewissenschafter, 47, 179 (1960).

(3) 

C. D. Hurd and C. D. Kelso, J. Amer. Chem. Soc., 62, 1548 (1940).

(4) 

E. Marcus, J. K. Chan and C. B. Strow, J. Org. Chem., 31, 1369 (1966).

Semi-Annual Research Report

James K. Hoyano

Since the last report work has continued in the investigation of the tin-tin coupling reaction of (transition-metal)tin compounds. In our hands these coupling attempts, which have been reported to undergo smoothly for a number of simple organotin derivatives, have been found to give very complex reaction products. Studies have also been initiated towards the selective synthesis of heteronuclear metal-metal bonds under non-ionic conditions utilizing some of the (transition metal)tin hydrides and (transition metal)germanium hydrides which have been recently prepared. Our findings of the tin-tin coupling reaction and the coupling of other metals to tin and to germanium are outlined below.

The Tin-Tin Coupling Reaction of (Transition Metal)Tin Compounds

With the successful isolation of some (transition metal)tin hydrides as outlined in the report of February 1972, it appeared likely that selective tin-tin couplings could be achieved of the general form:

$$(R)M-\overset{|}{\underset{|}{Sn}}-H \quad + \quad N-\overset{|}{\underset{|}{Sn}}-R(M) \longrightarrow (R)M-\overset{|}{\underset{|}{Sn}}-\overset{|}{\underset{|}{Sn}}-R(M) \quad + \quad \overset{|}{\underset{|}{N}}-H$$

(M=transition metal moiety)

These reactions have been reported (see February report for references) to go under mild conditions and high yields for simple organotin derivatives.

Since the last report two new (transition metal)tin hydrides have isolated and characterized.

$$ClMe_2SnMn(CO)_5 \quad + \quad (i\text{-}Bu)_2AlH \longrightarrow HMe_2SnMn(CO)_5$$

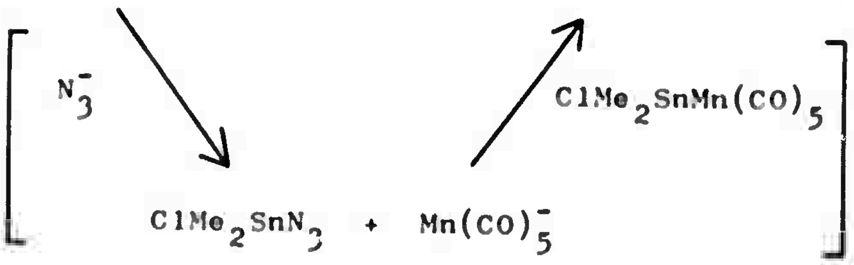
$$ClPh_2SnRe(CO)_5 \quad + \quad (i\text{-}Bu)_2AlH \longrightarrow HPh_2SnRe(CO)_5$$

Besides the azide $Cp(CO)_3WSnPh_2N_3$ reported previously, the compound $(CO)_5MnSnPh_2N_3$ has also been isolated as a crystalline air-stable solid.

$$ClPh_2SnMn(CO)_5 \quad + \quad NaN_3 \longrightarrow N_3Ph_2SnMn(CO)_5 \quad + \quad NaCl$$

However, attempts to prepare the methyl analogue resulted in a different course.

$$ClMe_2SnMn(CO)_5 \quad + \quad NaN_3 \longrightarrow Me_2Sn\left[Mn(CO)_5\right]_2$$



Apparently the azide ion displaces the $Mn(CO)_5^-$ ion and the reaction then proceeds as shown above. This is a general problem of ionic reactions for metal-metal bond forming and results in displacement of the most stable anion in the forward reaction. This factor can be overcome by using reactions such as described later in this report.

With the (transition metal)tin - hydrides and - azides already in hand along with simple known organotin - hydrides and - azides, tin-tin couplings were attempted with the expected course shown below.[1]

$$(R)M-\overset{|}{\underset{|}{Sn}}-N_3 \quad + \quad H-\overset{|}{\underset{|}{Sn}}-R(M) \quad \longrightarrow \quad (R)M-\overset{|}{\underset{|}{Sn}}-\overset{|}{\underset{|}{Sn}}-R(M) \quad + HN_3$$

When a 1:1 mole ratio of $(CO)_5MnSnPh_2N_3$ and $HSnPh_3$ were heated together neat or in solution reaction did not occur until ca. 90-100°. It was found that although all the $HSnPh_3$ had been consumed, a considerable amount of the starting azide remained unreacted (from the ir spectrum). The gas given off was ammonia and not HN_3. By adding more $HSnPh_3$ it was found that 3 moles were required to consume all of the azide and appeared to give the overall reaction shown below.

$$(CO)_5MnSnPh_2N_3 \quad + \quad 3HSnPh_3 \quad \xrightarrow{90-100^\circ} \quad NH_3 \quad + \quad N_2 \quad Ph_3Sn-SnPh_3 \quad + \quad '(CO)_5MnSnPh_2-SnPh_3'$$

The above reaction likely goes through the intermediate

"$(CO)_5SnPh_2$-NH-$SnPh_3$" whose reactive tin-nitrogen bonds are cleaved by the $HSnPh_3$ in a faster competing reaction than reduction of further quantities of the azide. Such a mechanism has been suggested for reactions of simple organotin azides with hydrides of silicon, germanium and tin.[2]

The hexaphenylditin from the above reaction was very difficult to separate because of similarities in solubilitiy, volatility and TLC retention time with the product(s). Furthermore, the infrared and TLC showed that at least three carbonyl compounds were present probably resulting from some type of disproportionation of the initially formed unsymmetrical coupled product. Similar intractable results were obtained when $Cp(CO)_3WSnPh_2N_3$ was reacted with $HSnPh_3$ or $HSnMe_3$ or when $(CO)_5MnSnPh_2H$ was reacted with N_3SnPh_3 or N_3SnMe_3.

The above azide reactions require fairly high temperatures and more reactive tin-nitrogen compounds such as the amides $-\overset{|}{\underset{|}{Sn}}-NR_2$ could possibly prevent the undesired side reactions. Although the (transition metal)tin amides such as $(CO)_5MnSnPh_2NR_2$ and $Cp(CO)_3WSnPh_2NR_2$ could not be isolated, the known simple organotin amides $Ph_3Sn-NEt_2$ and $Me_3Sn-NEt_2$ were readily prepared.[3] The reaction of these latter amides with various (transition metal)tin hydrides were examined. Reactions occurred at 20-30° to eliminate $HNEt_2$; however, as shown below, workup yielded mixtures of unexpected products. No tin-tin coupled products with appended transition metals were isolated.

$$(CO)_5MnSnMe_2H + Et_2NSnPh_3 \longrightarrow HNEt_2 + Ph_3Sn{-}SnPh_3 + Ph_3SnMn(CO)_5$$

$$(CO)_5MnSnPh_2H + Et_2NSnPh_3 \longrightarrow HNEt_2 + Ph_3Sn{-}SnPh_3 + Ph_3SnMn(CO)_5$$

$$(CO)_5MnSnPh_2H + Et_2NSnPh_3 \longrightarrow HNEt_2 + Ph_3Sn{-}SnPh_3 + Me_3SnMn(CO)_5$$

Although other compounds were present in the reaction mixtures, the above equations only show isolated and unambiguously identified compounds.

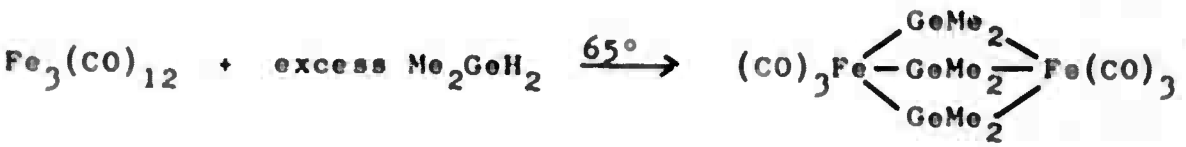
At the moment the above reactions for tin-tin coupling do not appear very promising for eventual application to the formation of a linear covalently bonded polymer. In a polymer of the type $-(Sn{-}M{-}Sn{-}Sn{-}M{-}Sn)_{\overline{n}}$ it appears that the tin-tin bond would be the weakest link; heteronuclear metal-metal bonds are usually stronger and more stable than homonuclear ones. A linear polymer containing alternating metals such as in $-(M{-}Sn)_{\overline{n}}$ or $-(M{-}Ge)_{\overline{n}}$ may be more readily synthesized besides being more stable. With this in mind some (transition metal)tin-hydrides and (transition metal)germanium-hydrides have been found to undergo selective heteronuclear metal-metal bond forming reactions which will now be described.

Metal-Metal Bond Forming Reactions of (Transition Metal)-Tin Hydrides and (Transition Metal)Germanium Hydrides

Recent reports in the literature have shown that organosilicon hydrides and organogermanium hydrides are of general utility for synthesizing covalently bonded silicon-(transition metal) and Germanium-(transition metal) compounds. Organotin hydrides have been used to a lesser extent probably because they give additional undesired side reactions. Some examples are given below.

$$2Ph_2SiH_2 + Co_2(CO)_8 \xrightarrow{25^\circ} 2HPh_2SiCo(CO)_4 + H_2$$ [4]

$$2Ph_3SiH + Mn_2(CO)_{10} \xrightarrow{160^\circ} 2Ph_3SiMn(CO)_5 + H_2$$ [5]



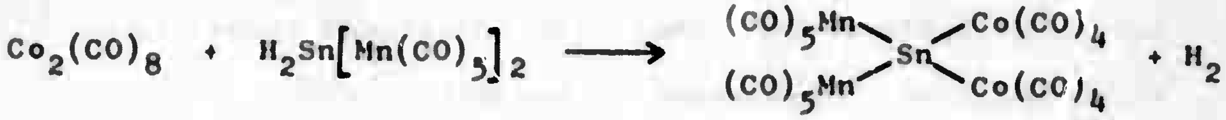
$$Fe_3(CO)_{12} + \text{excess } Me_2GeH_2 \xrightarrow{65^\circ} (CO)_3Fe(GeMe_2)_3Fe(CO)_3$$ [6]

$$PhGeH_3 + 1\tfrac{1}{2}Co_2(CO)_8 \xrightarrow{25^\circ} PhGeCo_3(CO)_{11} + 1\tfrac{1}{2}H_2 + CO$$ [7]

$$Me_3SnH + Fe(CO)_5 \xrightarrow{100^\circ} (Me_3Sn)_2Fe(CO)_4 + [Me_2SnFe(CO)_4]_2 + Me_4Sn_3Fe_4(CO)_{14} + Sn[Fe(CO)_4]_4$$ [8]

If reactions of the type given above can be applied to (transition metal)tin hydrides and (transition metal)-germanium hydrides, it would be potentially useful for application to the intermetallic polymer synthesis. No reactions of this type have been reported because the first (transition metal)tin hydrides have been only recently prepared in this laboratory and just a few (transition metal)germanium hydrides are known. Our results so far in the last few months on reactions of this type have been very promising.

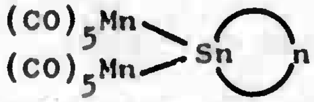
Cobalt carbonyl reacted smoothly with $H_2Sn[Mn(CO)_5]_2$ at room temperature



dark-red crystalline solid

The product $[(CO)_5Mn]_2Sn[Co(CO)_4]_2$ has been fully characterized (ir, full elemental analysis, molecular weight). There are only a few examples in which four transition metals are covalently bonded to one tin atom. Most previous attempts to prepare tetrametal substituted compounds of tin have relied on the nucleophilic displacement of halides by metal anions; unless the anions are very nucleophilic the fourth halogen usually cannot be displaced.[9] For example, the failure to prepare $Sn[Mn(CO)_5]_4$ by reacting $SnCl_4$ with excess $Mn(CO)_5^-$ may be due to the nucleophilic character of the anion and not because of steric factors as has been suggested.[10] Another complicating factor of ionic reactions is that metal exchange may occur if one attempts to bond two different metals to tin. The above hydride reaction appears to have none of the drawbacks of the ionic reactions.

When $H_2Sn[Mn(CO)_5]_2$ and $Mn_2(CO)_{10}$ were heated together at 90-100°, decomposition of the tin hydride occurred before reaction with the $Mn_2(CO)_{10}$ could take place. Elemental analysis of the red solid indicated that a cyclic oligomer of the form



had been formed. Since the simple (transition metal)tin hydrides such as $HPh_2SnMn(CO)_5$ and $HMe_2SnMn(CO)_5$ were fairly unstable and difficult to prepare in appreciable amounts, attention was directed to the hopefully more workable germanium analogs. However, some work is continueing with the tin complexes using the more stable rhenium derivatives.

The first germanium hydride carrying both a transition metal and an organic group, $HPh_2GeMn(CO)_5$, has been prepared in 80-90% isolated yield by the reaction sequence shown below.

$$\begin{tikzcd}
\mathrm{Mn(CO)_5^-} + \mathrm{Ph_2GeCl_2} \arrow[r] & \mathrm{ClPh_2GeMn(CO)_5} + \mathrm{Cl^-} \arrow[dl, "(\underline{i}\text{-Bu})_2AlH"] \\
\mathrm{HPh_2GeMn(CO)_5} &
\end{tikzcd}$$

(colorless, moderately air-stable oil)

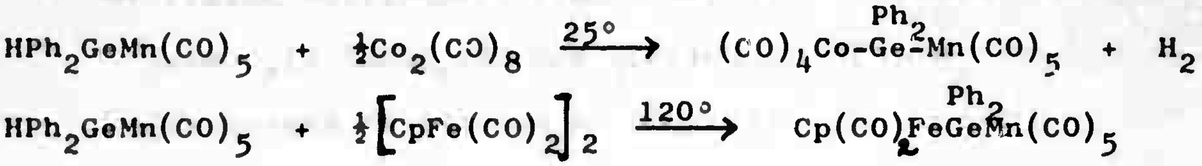
The coupling of this germanium hydride has been effected.

$$HPh_2GeMn(CO)_5 + Et_2NSnPh_3 \xrightarrow{30°} Et_2NH + Ph_3Sn\overset{Ph_2}{Ge}Mn(CO)_5$$

(white crystals)

Unlike the reactions with the tin hydrides, although some $Ph_3Sn\text{-}SnPh_3$ was formed, the reaction went cleanly and gave $Ph_3Sn\text{-}GePh_2\text{-}Mn(CO)_5$ as the only carbonyl compound (characterized by ir, elemental analysis, molecular weight).

Reactivity towards transition metal carbonyl dimers also appears favorable.



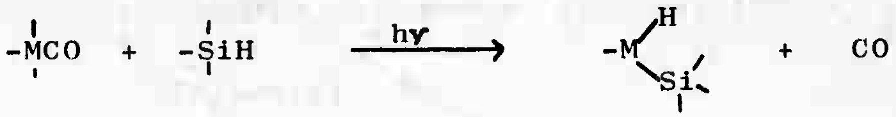
$$HPh_2GeMn(CO)_5 + \tfrac{1}{2}Co_2(CO)_8 \xrightarrow{25^\circ} (CO)_4Co\text{-}\overset{Ph_2}{Ge}\text{-}Mn(CO)_5 + H_2$$

$$HPh_2GeMn(CO)_5 + \tfrac{1}{2}\left[CpFe(CO)_2\right]_2 \xrightarrow{120^\circ} Cp(CO)_2Fe\overset{Ph_2}{Ge}Mn(CO)_5$$

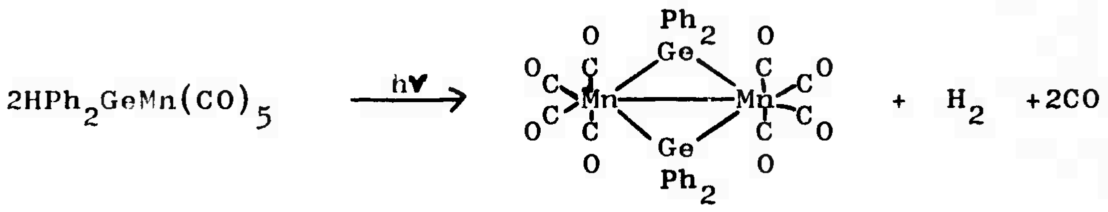
From the reactions studied so far there appears to be no rearrangement or disproportionation of the metal-metal bonds; for example in the first case above no $Ph_2Ge\left[Mn(CO)_5\right]_2$ was detected. It appears that the reactions proceed selectively.

Reaction of $HPh_2GeMn(CO)_5$ with other transition metal complexes and with metal-metal bonded main group dimers such as $Me_3Sn\text{-}SnMe_3$ is in progress to determine if the reaction can be generalized. Also the hydrides $H_2Ge\left[Mn(CO)_5\right]_2$[11] and $HPh_2GeRe(CO)_5$ have been prepared by $(\underline{i}\text{-}Bu)_2AlH$ reduction of the corresponding chlorides and the study of their reactions will be started shortly. Some recently reported (transition metal)germanium trihydrides $H_3GeRe(CO)_5$,[12] $H_3GeMn(CO)_5$,[13] $H_3GeCo(CO)_4$,[14] and $H_3GeGeH_2\text{-}Mn(CO)_5$[15] are also candidates for possible study of the metal-metal bond forming reactions.

The photochemical reaction of silicon hydrides with transition metal carbonyls has been found to be a general method for preparing silicon-(transition metal) bonds.[16]



Germanium hydrides will likely undergo similar reactions but the more unstable germyl(transition metal) hydride intermediates will probably not be isolable. However, (transition metal)-germanium bonded compounds should still be obtained after transformation of the initially formed unstable intermediate. The compound $HPh_2GeMn(CO)_5$ contains the germanium hydride and the metal carbonyl on the same molecule; photochemical irradiation in hexane solution gave the cyclic dimer in good yield.



(yellow crystals)

The silicon analog of $[(CO)_4MnGePh_2]_2$ has been shown by X-ray crystallography [17] to possess the D_{2h} structure shown above and also the presence of the Mn-Mn bond.

If the trans germaniums in the rigidly held cluster of $[(\mathrm{CO})_4\mathrm{MnGePh}_2]_2$ can be functionalized, a suitable monomer for the polymer synthesis may be obtained. A possible route is shown below.

$$\begin{tikzcd}
{[\mathrm{Ph}_2\mathrm{GeMn}(\mathrm{CO})_4]_2 + \mathrm{HCl}\ (\text{or } \mathrm{Cl}_2)} \arrow[r] & {[\mathrm{Cl}_2\mathrm{GeMn}(\mathrm{CO})_4]_2} \arrow[dl, "(\underline{\mathrm{i}}\text{-}\mathrm{Bu})_2\mathrm{AlH}"] \\
{[\mathrm{H}_2\mathrm{GeMn}(\mathrm{CO})_4]_2} &
\end{tikzcd}$$

Photochemical irradiation of $\mathrm{H}_3\mathrm{GeMn}(\mathrm{CO})_5$ may lead directly to $[\mathrm{H}_2\mathrm{GeMn}(\mathrm{CO})_4]_2$. Irradiation of $\mathrm{H}_2\mathrm{Ge}[\mathrm{Mn}(\mathrm{CO})_5]_2$ may give a similar compound. These photochemical reactions are currently being investigated.

Experimental Section

A dry nitrogen or argon atmosphere was maintained during all reactions and during work-up by using Schlenk apparatus. All solvents and reagents were dried or purified when necessary by standard procedures. Infrared spectra were recorded on Perkin-Elmer Models 457 or 421 grating spectrometers. Nuclear magnetic resonance spectra were obtained with a Varian T-60 instrument. Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Microanalyses were performed by the microanalytical laboratory of this department. Ultraviolet irradiations were carried out using a Hanovia Utility Lamp (Model 30620, 140 watts) at a distance of about 10 cm from a quartz flask containing the reaction mixture; the solution was maintained below room temperature during irradiation by means of a water-cooled cold finger.

(Diphenylhydridotin)pentacarbonylrhenium, $HPh_2SnRe(CO)_5$. A stirred mixture of $ClPh_2SnRe(CO)_5$ (0.23 g, 0.36 mmol) in 4 ml of hexane was treated with (i-Bu)$_2$AlH (0.5 ml of a 1 M heptane solution, 0.5 mmol). After stirring 10 minutes the yellow solution was filtered through a short silica gel column with 30 ml of benzene. Evaporation of the pale-yellow filtrate and molecular distillation of the residue at 70°/0.05 mm yielded 0.10 g (70%) of $HPh_2SnRe(CO)_5$ as a colorless oil: ir (hexane) 2113mw, 2014vs, 2005m, and

1780w (Sn-H); nmr (C_6D_6) τ 6.40 (singlet).

Anal. Calcd for $C_{17}H_{11}O_5SnRe$: C, 34.1; H, 1.84. Found: C, 34.8; H, 1.95.

(Dimethylhydridotin)pentacarbonylmanganese, $HMe_2SnMn(CO)_5$. This compound was prepared in a manner similar to the above. The isolated yield of $HMe_2SnMn(CO)_5$ was 30%; ir (hexane) 2095m, 2030w, 2005s, and 1997vs.

(Diphenylazidotin)pentacarbonylmanganese, $HPh_2SnMn(CO)_5$. A solution of $ClPh_2SnMn(CO)_5$ (1.50g, 3.00 mmol) in 125 ml of ether and a solution of NaN_3 (0.30g, 4.6 mmol) in 50 ml of water were shaken together in a 250 ml separatory funnel for 10 minutes. The ether layer was separated, dried over sodium sulfate and then evaporated to give a pale-yellow solid which was crystallized from hexane-benzene to yield 1.05 g (68%) of white crystals: mp 91-93°; ir (hexane) 2107m (azide), 2078m, and 2010s.

Anal. Calcd for $C_{17}H_{10}O_5N_3MnSn$: C, 40.02; H, 1.98; N, 8.24. Found: C, 40.36; H, 2.03; N, 8.07.

Bis(pentacarbonylmanganese)bis(tetracarbonylcobalt)tin(IV), $[(CO)_5Mn]_2Sn[Co(CO)_4]_2$ ---The dihydride $H_2Sn[Mn(CO)_5]_2$ (0.20 g, 0.39 mmol) and freshly sublimed $Co_2(CO)_8$ (0.13 g, 0.38 mmol) were stirred together in 10 ml of hexane until gas evolution (H_2) ceased (6 hours). Solvent was removed at reduced pressure and the residue was crystallized from dichloromethane-hexane to afford dark-red crystalf (0.25 g) of the product: mp 105-108° decomp.; ir(hexane) 2083s, 2065vs, 2048s, 2040msh, 2020 vs, and 2000m cm^{-1}; molecular weight found in CH_2Cl_2 solution was 830, calculated 853.

Anal. Calcd for $C_{18}O_{18}SnMn_2Co_2$: C, 25.40; H, 0.0; Sn, 13.95; Mn, 12.95; Co, 13.85. Found: C, 24.43; H, 0.17; Sn, 14.6; Mn, 13.3; Co, 13.9.

(Diphenylchlorogermanium)pentacarbonylmanganese, $ClPh_2GeMn(CO)_5$ --- A solution of $NaMn(CO)_5$ (prepared from 3.0 g (7.7 mmol) of $Mn_2(CO)_{10}$ and excess sodium amalgam) in 30 ml of tetrahydrofuran was added to a -78° solution of Ph_2GeCl_2 (4.6 g, 15.4 mmol). With stirring the reaction mixture was allowed to come to room temperature over one hour; the mixture was then stirred overnight. The reaction mixture was evaporated to dryness followed by extraction of the residue with 100 ml of chloroform. Evaporation of the chloroform provided a pale-yellow solid which, wher crystallized from hexane, afforded white needles (6.0 g, 95%) of the product: mp 103-104°; ir (hexane) 2108m, 2045w, 2018vs, and 2008ms cm^{-1}.

Anal. Calcd for $C_{17}H_{10}O_5ClGeMn$: C, 44 65; H, 2.21; Cl, 7.75. Found: C, 44.93; H, 2.32; Cl, 8.49.

(Diphenylhydridogermanium)pentacarbonylmanganese, $HPh_2GeMn(CO)_5$ --- A solution of $ClPh_2GeMn(CO)_5$ (1.55 g, 3.68 mmol) and 4 ml of the 1 M (i-Bu)$_2$AlH solution (4 mmol) in 10 ml of hexane was stirred for 18 hours. The yellow solution was filtered through a 10 g silicic acid column with 50 ml of benzene. The yellow filtrate was evaporated leaving a yellow oil which was distilled with a molecular distillation apparatus (50°/0.05 mm) to afford 1.10g (65%) of a pale-yellow oil: ir 2096ms, 2000vs cm^{-1}; nmr ($CDCl_3$) τ2.2-2.9 (multiplet, 10H, phenyl) and 4.77 (singlet, 1H, Ge-H).

Anal. Calcd for $C_{17}H_{11}O_5GeMn$: C, 48.3; H, 2.61. Found: C, 48.5; H, 2.70.

Preparation of $Ph_3Sn-GePh_2-Mn(CO)_5$ --- A solution of $HPh_2GeMn(CO)_5$ (0.50 g, 1.2 mmol) and Et_2NSnPh_3 (0.55 g, 1.3 mmol) in 5 ml of hexane was stirred for three hours at room temperature. Evaporation of the solvent followed by stirring of the residual oil overnight under vacuum resulted in the formation of a pale-yellow solid. Fractional crystallization from hexane yielded first $Ph_3Sn-SnPh_3$ (0.07 g) and then pale-yellow crystals of pure $Ph_3SnGePh_2Mn(CO)_5$ (0.30 g): ir (hexane) 2096ms, 2008s, and 2000vs cm^{-1}; molecular weight found in benzene solution was 769, calculated 771.

Anal. Calcd for $C_{35}H_{25}O_5SnGeMn$: C, 54.46; H, 3.27; Sn, 15.38. Found: C, 54.83; H, 3.51; Sn, 15.8.

Preparation of $(CO)_5MnGePh_2Co(CO)_4$ --- A solution of $HPh_2GeMn(CO)_5$ (0.30 g, 0.71 mmol) and freshly sublimed

$Co_2(CO)_8$ (0.12 g, 0.35 mmol) in 10 ml of hexane was stirred for 3 hours; the original dark solution gradually changed to yellow with deposition of a yellow solid. Evaporation of the solvent and crystallization of the residue gave yellow crystals (0.230 g) of the product: mp 146-148° (with decomposition); ir (hexane) 2101m, 2076ms, 2036w, 2015vs, 2010vs, 2002ms, 1005ms, and 1983w cm^{-1}.

Anal. Calcd for $C_{21}H_{10}O_9MnGeCo$: C, 42.54; H, 1.70; Mn, 9.27; Co, 9.94. Found: C, 42.64; H, 1.92; Mn, 9.04; Co, 9.72.

<u>Irradiation of $HPh_2GeMn(CO)_5$</u> --- A solution of $HPh_2GeMn(CO)_5$ (0.25 g, 0.59 mmol) in 50 ml of hexane was irradiated with uv light for 3 hours. The solvent was removed at reduced pressure and the residue was crystallized from hexane-chloroform to yield yellow crystals (0.15 g) of $[Ph_2GeMn(CO)_4]_2$: ir (hexane) 2042ms, 2001vs, 1974ms, and 1964s cm^{-1}.

Anal. Calcd for $C_{16}H_{10}O_4GeMn$: C, 48.79; H, 2.56. Found: C, 48.05; H, 2.69.

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17. The Mn-Mn distance in $[Ph_2SiMn(CO)_4]_2$ is 2.87Å (determined by L. F. Dahl, University of Wisconsin) and the Re-Re distance in $[Ph_2SiRe(CO)_4]_2$ is 3.00Å (determined by T. E. Haas, Tufts University).

Research Report

Don Murphy

Work on the [[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)]rhodium Rh(DO)(DOH) system has continued.[1] The schemes for preparation of metallic polymers using this system have been outlined previously.[2] Functionalized tin moieties held in <u>trans</u> positions on rhodium by the tetradentate planar ligand would be polymerized using coupling reactions being developed by J. Hoyano.[3]

As noted in the last report,[1] the bis triphenyltin complex was prepared, but the tin rhodium bonds proved susceptible to electrophilic reagents preventing functionalization.

Interest during the past period has centered around the square Rh(I) complex Rh(DO)(DOH), **2**, obtained from the <u>trans</u> dichloro, **1**, by reduction with basic ethanol.

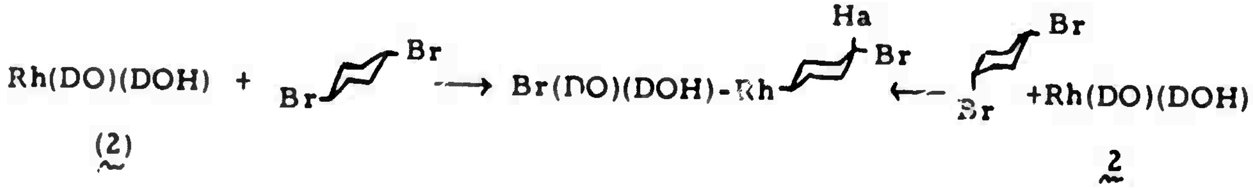
$$\underset{\mathbf{1}}{\underline{t}\ Cl_2\ Rh(DO)(DOH)} \xrightarrow[H_2O]{OH^-,\ EtOH} \underset{\mathbf{2}}{Rh(DO)(DOH)}$$

The Rh(I) complex forms as tiny green-gold crystals with a high reflectivity suggestive of metal-metal interaction in the solid, common for square planar complexes of Rh, Ir, and Pt. Single crystals were grown from hot acetonitrile, and Fleischer has recently completed a single crystal X-ray structure determination. He found isolated molecules well separated in the solid. The luster is apparently due to the macrocyclic ligand as is found with many porphyrin complexes.

The planar **2** is a very reactive d^8 system toward oxidative addition reactions.[4] The reaction involves addition of the elements of a molecule X-Y to a metal center to increase the coordination number and oxidation state of the metal by two.

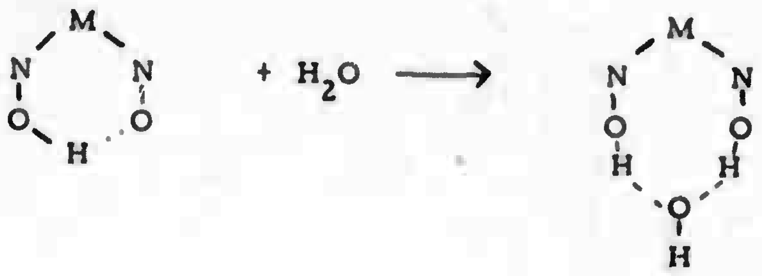
$$X - Y + ML_n \longrightarrow ML_nXY$$

The detailed mechanism, both at the metal and at carbon, has not been completely established. The reactivity and geometrical constraints of this rhodium complex appear suitable to give some insignt into the oxidative addition reaction. The unsaturated **2** gave <u>trans</u> addition products for a variety of alkyl halides (MeI, EtI, $C_6H_{11}Br$, and $C_6H_5CH_2Cl$), acid chlorides (CH_3COCl and C_6H_5COCl), and halogens (I_2 and Br_2). The reactivity towards secondary bromides seemingly would allow a test of stereochemistry at carbon. Following the work of Jensen[5] on the cobalt(I) anions, treatment with <u>cis</u> and <u>trans</u> 1,4-dibromocyclohexanes apparently gave only the <u>trans</u> cyclohexyl ring. The products from the two reactions were identical by nmr (δ 4.6 (S, 1H, H_a)).

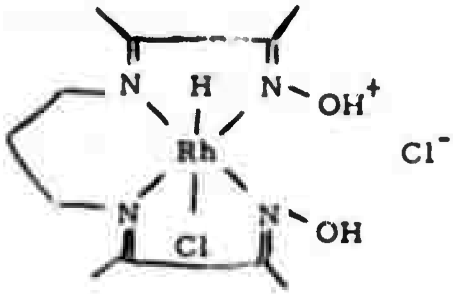


The region in which the vicinal proton of the <u>cis</u> product would be expected (δ 3.5 - 4.2) was obscured by methylene protons on the ligand, so that *cis* content could be inferred only by difference. The most obvious mechanism to account for loss of stereochemistry is a radical mechanism. a radical process is discounted by the lack of inhibition produced by hydroquinone and the order of reactivity (primary > secondary, tertiary does not react). A metal displacing metal mechanism shown to exist for anionic cobalt nucleophides[6] remains a possibility.

The stereochemistry of oxidative addition at metal centers is also a matter of interest. Substrates such as alkyl halides, acid chlorides, and halogens apparently form both *cis* and *trans* metal complexes, whereas hydrogen, olefins and acetylenes form only *cis* complexes. The possibility exists that *trans* addition products are formed by a rapid isomerization of an initially formed *cis* complex. The DOH system would appear to exclude that possibility. Hydrogen, etheylene, and acetylene do not add to the planar **2**. Stronger *cis* bonding ligands do, however, form addition complexes. Tetracyanoethylene, dimethylacetylene-dicarboxylate, and dimethyl furmarate readily formed addition products in THF. Models indicated that four non planar positions could be spanned by the DOH ligand system, but with considerable strain. The dimethylacetylenedicarboxylate complex showed two methyl resonances in the nmr for the ester methyls (δ 3.35 and 3.45) and four resonances for ligand methyl groups (δ 1.60, 1.70, 1.90, and 2.15), consistent with such geometry. The planar ligand shows two closely spaced singlets for ligand methyls (2.25δ). The non planar complexes are hygroscopic. A water molecule could interact with the oxime bridge to effectively lengthen the bridge and relieve strain as illustrated.



The oxime bridge can interfere in other reactions as well. Excess dry hydrogen chloride gave a hydride 3 in which the oxime bridge has been opened,

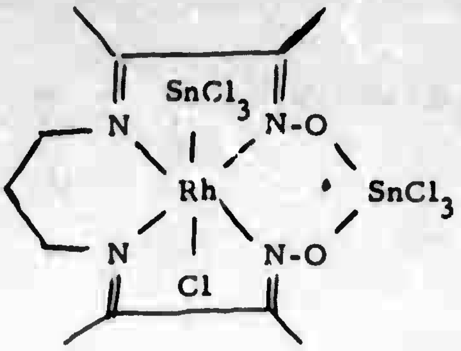


$\nu_{\text{Rh-H}} = 2030\ \text{cm}^{-1}$

3

as evidenced by a broad OH stretch around 2500 cm^{-1}.[7] Upon standing, the hydride disappeared and the oxime bridge closed to give the original dichloride 1. One equivalent of hydrogen chloride gave a normal addition product ($\nu_{\text{Rh-H}} = 2065$), but upon standing the hydride disappeared and the oxime bridge opened.

Stannic chloride gave an addition product with the unsaturated 2 which analyzed for Rh(DO)(DOH)Sn_2Cl_7, 4. The structure probably involves an $SnCl_3$ in the bridge.



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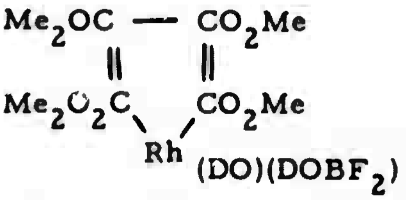
Treatment of the dichloride **1** with boron trifluoride etherate gave the BF_2 bridged species, **5**, analogous to dimethylglyoxime complexes by Schrauzer.[8] Reduction with basic ethanol gave the Rh(I) complex, **6**, with a BF_2 bridge. It was hoped that the BF_2 group would strengthen the ligand system and prevent *cis* bonding ligands from forming adducts. Dimethylacetylenedicarboxylate still formed a *cis* adduct, although the nmr indicates two acetylenes per rhodium, possibly in a metallocycle, **7**.



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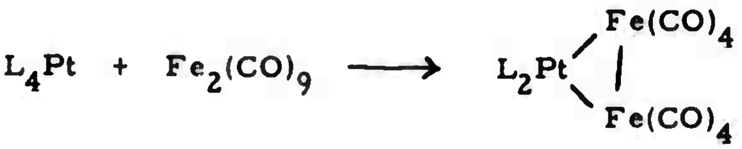
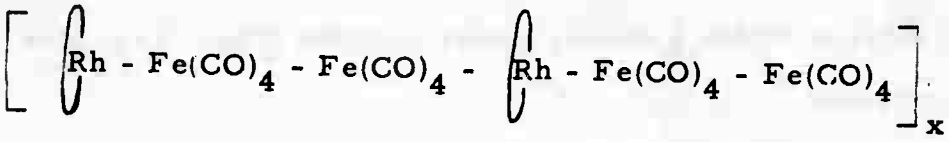
An interesting version of the oxidative addition reaction was recently reported[9] in which tetrakistriphenylphosphine platinum and iron enneacarbonyl gave the cluster **8**.



$$L_4Pt + Fe_2(CO)_9 \longrightarrow L_2Pt\begin{matrix} Fe(CO)_4 \\ | \\ Fe(CO)_4 \end{matrix}$$

8

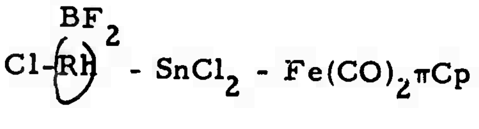
Such a reaction with the DOH system could conceivably give a polymer,



$$\left[Rh - Fe(CO)_4 - Fe(CO)_4 - Rh - Fe(CO)_4 - Fe(CO)_4 \right]_x$$

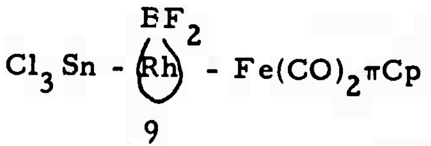
The proton bridged 2 upon treatment with iron enneacarbonyl gave a paramagnetic complex containing one iron per rhodium and giving three ir peaks in the CO region. The iron apparently inserted in the bridge. The BF_2 bridged complex did not react.

The iron tin species $\pi Cp(CO)_2Fe\text{-}SnCl_3$ gave an orange addition product with the BF_2 bridged complex. The maintenance of the iron tin bond in the product has not been demonstrated. An alternative product which cannot be excluded on the basis of empirical formula is the inserted complex 9.



$$Cl-\overset{BF_2}{Rh}-SnCl_2-Fe(CO)_2\pi Cp$$

or



$$Cl_3Sn-\overset{BF_2}{Rh}-Fe(CO)_2\pi Cp$$

9

The protonbridged complex 2 does not give an isolable product, presumably due to insertion of the tin in the bridge.

The nonrigidity of the DOH ligand system and the reactivity of the oxime bridge have hampered development of the Rh(DO)(DOH) system. Replacing the proton in the oxime bridge by boron apparently alleviates reactivity problems at the bridge. To make a truly rigid planar system, it appears that a synthetically more complicated ligand more nearly approaching the biological porphyrins is required.

Experimental

The dichloro complex **1** and the planar complex **2** were prepared as previously reported.[1]

Trans-methyliodo[[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)] rhodium. The d^8 complex **2** (100 mg, 0.29 mmol) was transferred into a round bottom flask in an inert atmosphere box and fitted with a rubber septum. Through the septum, THF (5 ml) was added followed by methyl iodide (20 μl, 0.31 mmol). A reddish yellow solution was rapidly formed from which the product precipitated as orange crystals. The crystals were filtered, washed with ether, then recrystallized from THF to give the product (130 mg, 86%): nmr (60 MHz in $CDCl_3$); δ 0.20 (d, J = 1.2Hz, 3H), δ 2.25 (S, 14H), δ 4.0 (M, 4H), δ 12.35 (S, 1H).

Anal. Calcd. for $RhC_{12}H_{22}N_4IO_2$: C, 29.77; H, 4.15; N, 11.57; I, 26.21. Found: C, 29.58; H, 4.47; N, 11.61; I, 25.24.

Trans-ethyliodo[[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)]rhodium. The above procedure yielded the ethyl iodide derivative as yellow crystals (63%): nmr (60 MHz in $CDCl_3$); δ 0.35 (d of t, J_t = 4 Hz, J_d = 0.8 Hz, 3H), δ 1.05 (d of q, J_q = 4 Hz, J_d = 1.4 Hz, 2H), δ 2.20 and 2.30 (S on M, 13H), δ 2.70 (M, 1H), δ 4.00 (M, 4H), δ 12.00 (S, 1H); nmr (100 MHz in $CDCl_3$); δ 0.26 (d of t J_t = 7 Hz, J_d = 1.5 Hz, 3 H), δ 0.94 (d of q, J_q = 7 Hz, J_d = 2 Hz, 2H), δ 2.26 and 2.32 (S on M, 13H), δ 2.70 (M, 1 H), δ 3.90 (d of q, J_q = 22 Hz, J_d = 8 Hz, 4 H), δ 12.05 (S, 1H).

Anal. Calcd. for $RhC_{13}H_{24}N_4IO_2$: C, 31.40; H, 4.81; N, 11.20; I, 25.50; Rh, 20.62. Found: C, 31.37; H, 4.76; N, 11.36; I, 25.13; Rh, 20.23.

Trans-cyclohexylbromo[[3'3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)]rhodium. The procedure as outlined was followed, but four hours reflux was required for completion of the reaction: nmr (60 MHz in $CDCl_3$); δ 0.60 to 1.6 (M, 11 H); δ 2.20 (S, 13 H); δ 2.90 (M, 1 H); δ 3.90 (M, 4 H); δ 12.40 (S, 1 H).

Anal. Calcd. for $RhC_{17}H_{30}BrN_4O_2$: C, 40.41; H, 5.98; N, 11.09; Br, 15.81. Found: C, 40.15; H, 5.92; N, 11.34; Br, 16.22.

Trans-(trans-4-bromocyclohexyl)bromo[[3, 3'-(trimethylenedinitrile)-di-2-butanone dioximato](1-)]rhodium. Both cis and trans 1,4 dibromocyclohexanes gave the same isomer in refluxing THF as evidenced by nmr: nmr (60 MHz in $CDCl_3$); δ 0.60 to 1.6 (M, 10H); δ 2.20 (S, 13 H); δ 2.90 (M, 1 H); δ 3.90 (M, 4 H); δ 4.6 (M, 1 H).

Anal. Calcd. for $RhC_{17}H_{29}Br_2N_4O_2$: C, 34.95; H, 5.00; N, 9.60; Br, 27.36. Found: C, 35.02; H, 5.01; N, 9.71; Br, 27.22.

Trans-benzylchloro[[3, 3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)]rhodium. Benzyl chloride in THF at room temperature gave the addition product as before: nmr (60 MHz in $CDCl_3$); δ 2.10 (S on M, 17H); δ 2.75 (M, 1 H); δ 3.80 (M, 4 H); δ 6.75 (M, 2 H), δ 7.05 (M, 3 H); δ 12.00 (S, 1 H).

Anal. Calcd. for $RhC_{18}H_{26}ClN_4O_2$: C, 46.10; H, 5.56; N, 11.95; Cl, 7.48. Found: C, 46.21; H, 5.67; N, 11.98; Cl, 7.75.

Trans-acetylchloro[[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)]rhodium. Acetyl chloride with **2** in THF gave the product (91%): nmr δ 2.0 (S, 3 H); δ 2.30 (S on M, 14 H); δ 4.0 (M, 4 H): ir $^{\nu}$CO = 1670 cm^{-1} (KBr).

Anal. Calcd. for $RhC_{13}H_{22}ClN_4O_3$: C, 37.20; H, 5.24; N, 13.30; Cl, 8.34; Rh, 23.16. Found: C, 36.34; H, 5.33; N, 13.33; Cl, 8.35; Rh, 23.1.

Trans-benzoylchloro[[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)]rhodium. Similar treatment with benzoyl chloride gave the product (78%): nmr (60 MHz in $CDCl_3$); δ 2.15 and 2.25 (S on M, 14 H); δ 4.00 (M, 4 H); δ 6.90 (M, 2 H) δ 6.90 (M, 2 H) δ 7.30 (M, 3 H); δ 9.05 (S, 1 H): ir $^{\nu}$C = O = 1650 cm^{-1} (KBr).

Anal. Calcd. for $RhC_{18}H_{24}ClN_4O_3$: C, 44.80; H, 4.97; N, 11.60; Cl, 7.95. Found: C, 44.26; H, 4.99; N, 11.76; Cl, 7.74.

Trans-dibromo[[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)rhodium. The procedure was modified by using ethanol as solvent to give the dibromide as yellow crystals after recrystallization from dichloromethane-ethanol.

Anal. Calcd. for $RhC_{11}H_{19}Br_2N_4O_2$: C, 26.32; H, 3.81; N, 11.16; Br, 31.83. Found: C, 26.11; H, 3.81; N, 11.09; Br, 32.06.

Reactions of cis Coordinating Ligands. The mild *cis* coordinators hydrogen, ethylene, and acetylene fail to react with the planar **2** to give an addition product. Hydrogen eventually formed a rhodium mirror at 100 psi and 100°C. Many of the strong *cis* coordinators did form addition complexes, destroying planarity of the $(DO)(DOH)_{pn}$ ligand system.

Dimethylacetylenedicarboxylate [[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)] rhodium. Freshly distilled dimethylacetylenedicarboxylate (30 μl, 0.33 mmol) was added to a THF suspension of the planar 2 (100 mg, 0.29 mmol) in THF (5 ml). The mixture rapidly turned orange, and an orange solid began to precipitate. The mixture was concentrated, ether added, filtered, and washed well with ether. The hygroscopic orange product (110 mg, 78%) was recrystallized from THF: nmr (60 MHz in $CDCl_3$); δ 1.60, 1.70, 1.90, and 2.15 (S on M, 14 H total); δ 3.35 and 3.45 (S on M, 10 H total); δ 5.65 (bds, 3 H); i.r. (KBr) $\nu_{C=O}$ = 1700 cm^{-1}, $\nu_{C=N}$ = 1575 cm^{-1}, ν_{N-O} = 1150 cm^{-1}.

Anal. Calcd for $RhC_{17}H_{25}N_4O_6$: C, 42.10; H, 5.10; N, 11.55. Found: C, 41.84; H, 5.24; N, 11.02.

Dimethylfumarate[[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)]rhodium. In the same way the dimethylfumarate adduct was prepared in 73% yield after recrystallization from dichloromethane hexane. This complex was too insoluble for nmr: i.r. (KBr); $\nu_{C=O}$ = 1730 cm^{-1}, $\nu_{C=N}$ = 1680 cm^{-1}, ν_{N-O} = 1150 cm^{-1}.

Anal. Calcd. for $RhC_{17}H_{27}N_4O_6$: C, 42.10; H, 5.16; N, 11.55. Found: C, 41.84; H, 5.24; N, 11.02.

Tetracyanoethylene[[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)]rhodium. Tetracyanoethylene gave a 97% yield of addition product. The complex was too insoluble to recrystallize and was analyzed crude: i.r. (KBr); $\nu_{C\ N} = 2180,\ 2080\ cm^{-1}$, $\nu_{C=N} = 1600\ cm^{-1}$, $\nu_{N\text{-}O} = 1130\ cm^{-1}$.

Anal. Calcd. for $RhC_{17}H_{19}N_8O_2$: C, 43.45; H, 4.04; N, 23.85. Found: C, 41.11; H, 4.20; N, 22.23.

Reactions of the Oxime Bridge

Reaction with hydrogen chloride. Bubbling dry, gaseous hydrogen chloride through a benzene suspension of the planar 2 (100 mg) gave a yellow solid which was filtered and washed with ether: i.r. (KBr pellet); $\nu_{O\text{-}H}$ 2400 (bd), $\nu_{Rh\text{-}H}$ 2030 cm^{-1}. The product after several hours under nitrogen spontaneously closed the oxime bridge, the hydride disappears and the dichloride **1** was formed.

Addition of one equivalent of dry hydrogen chloride in benzene gave an orange solid which was filtered and washed with ether: i.r. (KBr pellet) ν_{OH} 3500 (bd), $\nu_{Rh\text{-}H}$ 2065 cm^{-1}. The oxime bridge was retained, but after several hours under nitrogen the hydride peak disappears and a broad band at 2500 cm^{-1} appears, indicating a hydride shift to open the bridge.

Trans-chlorotrichlorotin[trichloro[[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)stannate]rhodium. The square **2** (100 mg, 0.29 mmol) was treated with stannic chloride in benzene (5 ml). An orange precipitate was rapidly formed which was filtered, washed with ether, and recrystallized from dichloromethane to yield the product (220 mg, 91%).

Anal. Calcd. for $RhSn_2C_{11}H_{18}Cl_7O_2$: C, 15.96; H, 2.31; N, 6.77; Cl, 29.98. Found: C, 16.05; H, 2.12; N, 6.85; Cl, 31.07.

Trans-dichloro[difluoro[[3,3'-(trimethylenedinitrilo)-di-2-butanone dioximate](1-)]borate]rhodium, 5. The rhodium(III) dichloride 1 (2.0 g, 4.85 mmol) in a diethyl ether (30 ml) suspension was treated with boron trifluoride etherate (4 ml, 32.5 mmol). The mixture was stirred for 12 hours to give a yellow powder, which was filtered and washed with ether in a Schlenk apparatus under nitrogen. The product was purified by soxhlet extraction with dichloromethane to give yellow needles (2.10 g, 94%): i.r.; $\nu_{C=N}$ = 1625, 1560 cm^{-1}, ν_{N-O} = 1125 cm^{-1}, ν_{B-O} = 1175, 800 cm^{-1}, ν_{B-F} = 1020, 995 cm^{-1}.

Anal. Calcd. for $RhBC_{11}H_{18}Cl_2F_2O_2$: C, 28.67; H, 3.94; N, 12.16; Cl, 15.38; F, 8.24; B, 2.35; Rh, 22.33. Found: C, 29.59; H, 4.79; N, 11.88; Cl, 14.85; F, 7.90; B, 2.22; Rh, 21.23.

[difluoro[[3,3'-trimethylenedinitrilo di-2-butanone dioximato](1-)] borate]rhodium, 6. The boron difluoride bridged dichloride (500 mg, 1.1 mmol) was treated with basic aqueous ethanol under the same conditions as the proton bridged 1 to give the analogous boron bridged rhodium(I) complex. The product is somewhat greener than 2. The air sensitive complex was characterized by its oxidative addition products. Oxidation by chlorine in acetonitrile gave a yellow solid identical to the dichloride by ir.

Trans-amyliodo[difluoro[[3, 3'-(trimethylenedinitrilo)-di-2-butanone dioximato](1-)]borate]rhodium. Addition of amyl iodide as before in THF gave, after recrystallization from THF the trans adduct (82%): nmr (60 MHz in $CDCl_3$); δ 0.50 to 1.40 (M, 11 H); δ 2.35 (S on M, 14 H total); δ 4.10 (M, 4H).

Anal. Calcd. for $RhBC_{16}H_{29}F_2IO_2$: C, 32.68; H, 4.97; N, 9.53; F, 6.46; I, 21.58. Found: C, 32.92; H, 5.39; N, 9.37; F, 6.46; I, 21.59.

Reaction of [difluoro[[3, 3'-(trimethylenedinitrile)-di-2-butanone diorimato](1-)borate]rhodium with dimethylacetylenedicarboxylate. Treatment of the boron bridged 6 (100 mg, 0.26 mmol) with dimethylacetylenedicarboxylate (100 ml, 1.1 mmol) gave a yellow product, 7, after recrystallization from THF. The rhodium picks up two of the acetylene molecules: nmr (60 MHz in $CDCl_3$); δ 1.75, 1.85, 2.00, and 2.25 (S on M, 14 H total); δ 3.50 and 3.60 (S on M, 16 H total). The complex could not be obtained in pure form.

Reaction of the boron bridged 6 with trichlorotindicarbonylcyclopentadienyl iron. The boron bridged 6 (230 mg, 0.59 mmol) was treated with trichlorotindicarbonyl cyclopentadienyl iron (300 mg, 0.75 mmol) in THF (5 ml). The mixture rapidly turned blue black then slowly turned orange. The mixture was stirred two days. The orange precipitate was filtered, washed well with THF, then recrystallized from dichloromethane to give orange crystals of the mono dichloromethane solvate, 9, (125 mg, 27%): i.r. (KBr); ν_{CO} = 2010, 1965 cm^{-1}.

Anal. Calcd. for Rh, Sn, Fe, C_{18}, H_{25}, B, Cl_5, F_2N_4, O_4: C, 26.02; H, 2.87; N, 6.39; Cl, 20.21; Sn, 13.53; Fe, 6.37; Rh, 11.73.

Found: C, 26.06; H, 2.92; N, 6.60; Cl, 20.17; Sn, 11.55; Fe, 5.43; Rh, 10.0.

Reaction of the planar **2** with diiron enneacarbonyl. The planar **2** (100 mg, 0.29 mmol) and diiron enneacarbonyl (100 mg, 0.28 mmol) were placed in a round bottom flask in an inert atmosphere box. THF (5 ml) was added and the reaction was stirred about two hours at room temperature and gave a purple solid which was then filtered under inert atmosphere and washed well with THF, ethanol, and ether. The product was analyzed crude: i.r. (KBr) ν_{CO} = 1985, 1915, and 1875 cm^{-1}.

Anal. Calcd. for $RhFeC_{14}H_{18}N_4O_5$: C, 34.95; H, 3.77; N, 11.65; Rh, 21.39; Fe, 11.61. Found: C, 32.18; H, 4.54; N, 12.69; Rh, 19.7; Fe, 11.45.

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Report on Research

Rex Stark

Introduction

As discussed in previous technical reports from this group,[1,2,3] we have been attempting to synthesize tin hydrides coordinated to transition metals, with the expectation that coupling reactions involving such hydrides might lead to desired metal-metal bonded polymers. Success in making the desired hydridotins has been limited, with only a half-dozen new compounds being reported.[1,2,3] Additional work by Dr. Hoyano has raised questions about the feasibility of subsequent coupling reactions. In searching for alternative routes to the desired polymers, it was decided to attempt metal-metal bond formation via redistribution reactions. Work in this area is continuing.

Hydridotin Transition Metal Complexes

Several attempts to synthesize new compounds having a tin hydride bonded to a transition metal have failed. π-Cp(CO)$_2$FeSnPh$_2$Cl was treated with i-Bu$_2$AlH in hexane. After passing the mixture through a silica column, nmr failed to show Cp or Sn-H resonances. It would appear that the reducing agent attacked the tin-iron bond.

The synthesis of $HPh_2SnMn(CO)_5$ has been previously reported.[1,3] Because of failure to synthesize any of the inexpensive hydridotin iron compounds,[3,4] it was felt that coupling reactions should be studied with the well characterized $HPh_2SnMn(CO)_5$. Large scale (1-2 gm) syntheses of this compound led to unsuspected difficulty, in that only a trace of the desired hydride was found, the major product being $Ph_3SnMn(CO)_5$.

Tris-(tetracarbonylcobalt)tin chloride was prepared from $Co_2(CO)_8$ and $SnCl_4$ in THF.[5] It had earlier been reported[2] that reduction of this compound led to $Co_4(CO)_{12}$ and unidentified products. Further study of this system shows that reduction with i-Bu_2AlH in hexane followed by chromatography on silica leads to a deep purple crystalline compound (mp 158-160d), pure by TLC, but which decomposes on standing for a day or so under argon. No protons were visible by nmr, but microanalysis indicated 1% hydrogen. It was originally believed that the product might be the dimer $[Co(CO)_4]_3SnSn[Co(CO)_4]_3$, but this is not the case. The product has not been identified.

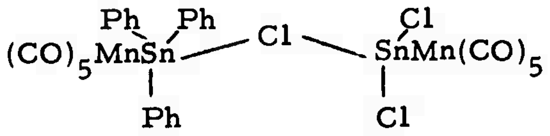
Reduction of $[Co(CO)_4]_2SnCl_2$ with one or two equivalents of hydride led only to crude air sensitive mixtures.

Redistribution Reactions

Redistribution (scrambling) reactions among organotins and organotin halides are a well known phenomenon. For example, R_4Sn with $SnCl_4$ may give R_2SnCl_2 or other products, dependent upon reaction conditions and proportions of reactants. One product predominates in the neat reaction, whereas in solution with a catalyst (eq. $AlCl_3$) a statistical mixture results. Analogous reactions might lead to metal-metal bond formation if the systems are chosen so that transfer of a transition metal from one group IV element to another is thermodynamically favored over transfer of alkyl or aryl groups or halides. Aryl-halogen exchange has been demonstrated by Gorsich.[6]

$$2\ Ph_3SnMn(CO)_5 + Cl_3SnMn(CO)_5 \longrightarrow 3\ Ph_2ClSnMn(CO)_5$$

This reaction goes cleanly and does not result in cleavagle of metal-metal bonds, indicating that ionic intermediates are not involved. A five-coordinate tin species may be the intermediate.



In two cases, both utilising transition metal silyls, Don Murphy has shown that metal group-halogen exchange does take place under suitable conditions.

$$Me_3SiMn(CO)_5 + Cl_3SnMn(CO)_5 \longrightarrow Me_3SiCl + Cl_2Sn[Mn(CO)_5]_2$$

$$\pi\text{-}Cp(CO)_2FeSiMe_3 + \pi\text{-}Cp(CO)_2FeSnCl_3 \longrightarrow Me_3SiCl + Cl_2Sn[\pi\text{-}Cp(CO)_2Fe]_2$$

If such reactions are found to be of general utility, the possibilities are limitless. If the five-coordinate transition state is correct, one drawback may be isolation of products, since the reactions should go better with increasing chloro substitution on tin. (It is known that R_3SnCl species remain four-coordinate even in polar solvents, whereas R_2SnCl_2 will often coordinate one or more solvent molecules.) Hopefully, monochlorotin species will undergo the desired reactions.

It may be that hydride transfer will lead to the type of compound desired, although utility in building up chains is doubtful since we would require as starting materials the same hydridotin transition metal compounds which have been difficult to prepare in the past.

$$R_3Si[M] + R_3SnH \longrightarrow ?$$

$$R_2SnH_2 \longrightarrow ?$$

$$R_2HSn[M] \longrightarrow ?$$

It has been reported[7] that $Me_2ClSnMn(CO)_5$ may be prepared by the overnight reaction of dimethyltin dichloride and $Mn(CO)_5^{\ominus}$ in THF, whereas workup an hour or so after mixing the reactants leads only to $Me_2Sn[Mn(CO)_5]_2$ and unreacted Me_2SnCl_2. As a preliminary step in our study of redistribution reactions, attempts were made to synthesize $Ph_2ClSnMn(CO)_5$ from Ph_2SnCl_2 and $Ph_2Sn[Mn(CO)_5]_2$. In THF solution the reaction was found to be very slow, proceeding ~ 5% after one day and perhaps 80% in one week. When mixed next at 140° for 1 - 2 hours, the starting materials were largely unreacted, the products being $Ph_2ClSnMn(CO)_5$ and $PhCl_2SnMn(CO)_5$. Thus the overnight reaction reported by Jetz[7] must require traces of $Mn(CO)_5^{\ominus}$ or some other species.

Trimethylsiliconcobalt tetracarbonyl was prepared from trimethylsilane and cobalt carbonyl.[8]

$$2\,Me_3SiH + Co_2(CO)_8 \longrightarrow 2\,Me_3SiCo(CO)_4 + H_2$$

With Ph_3SnH, neat, this compound gave inconclusive results. Decomposition of the products was evident, and some hexaphenylditin was present.

$$Me_3SiCo(CO)_4 + Ph_3SnH \longrightarrow ?$$

A neat reaction of $Me_3SiCo(CO)_4$ with $Cl_2Sn[Co(CO)_4]_2$ yielded no crystalline products, but infrared spectroscopy showed that some $ClSn[Co(CO)_4]_3$ was present.

$$Me_3SiCo(CO)_4 + Cl_2Sn[Co(CO)_4]_2 \not\longrightarrow Me_3SiCl + ClSn[Co(CO)_4]_3$$

$Me_3SiFe(CO)_2Cp$ was prepared from $Fe(CO)_2Cp^-$ and Me_3SiCl.[9] Neat reaction with $Ph_2ClSnFe(CO)_2$ for 1 hour at 100° gave mainly starting material. This will be repeated using a longer reaction time.

$$Me_3SiCl + Fe(CO)_2Cp^{\ominus} \longrightarrow Me_3SiFe(CO)_2Cp$$

$$Me_3SiFe(CO)_2Cp + Ph_2ClSnFe(CO)_2Cp \xrightarrow[1\text{ hour}]{100^\circ} NR$$

Further study of these redistribution reactions might include the following.

$$[\pi\text{-}Cp(CO)_2Fe]_2SnPh_2 + Ph_2SnCl_2 \xrightarrow{?} Ph_2ClSnFe(CO)_2Cp$$

$$2\,Me_3SiFe(CO)_2Cp + Cl_3SnFe(CO)_2Cp \xrightarrow{?} 2\,Me_3SiCl + ClSn[Fe(CO)_2Cp]_3$$

$$Me_3SnMn(CO)_5 + Cl_3SnMn(CO)_5 \xrightarrow{?} \text{see if Me or Mn is exchanged with Cl}$$

$Me_3SiMo(CO)_3Cp$ + Ph_2SnCl_2, Ph_3SnCl, $Me_2ClSnMo(CO)_3Cp$ or
$MeCl_2SnMo(CO)_3Cp \longrightarrow$?

$Me_3SiMn(CO)_5$ + $Ph_2ClSnMn(CO)_5$ or another tin species $\longrightarrow$?

It is possible that these reactions will be more facile if the less stable transition metal-lead compounds are used as starting materials instead of the silanes.

Experimental

Reduction of $Ph_2ClSnFe(CO)_2Cp$

$Ph_2ClSnFe(CO)_2Cp$ (20 mg, .0412 mmole) was placed in 1 cc hexane under argon. A heptane solution of i-Bu_2AlH (1.04 M, 60 μl, 50% excess) was added slowly at room temperature. The insoluble starting compound dissolved over ~5 minutes to form an orange solution. After stirring 2 hours, the solution was passed through a degassed silica column on benzene. Nmr of the yellow eluant indicated no Sn-H or π-Cp resonances.

Reduction of $Ph_2ClSnMn(CO)_5$

To a degassed hexane solution of $Ph_2ClSnMn(CO)_5$ (1.512 gm, 3 mmole) was added, over 15 minutes at room temperature, 3 ml i-Bu_2AlH (1.04 M in heptane). After stirring 3 hours the solution was passed through a degassed silica column on benzene. Evaporation of the solvent gave a solid residue of 3-4 components. This was triturated in a small amount of hexane, and a white solid was filtered off. This was shown by ir and microanalyses to be $Ph_3SnMn(CO)_5$. The remaining material was eluted from a silica column with 15% benzene-hexane. Distillation of the first fraction yielded a few drops of the desired hydride, and additional $Ph_3SnMn(CO)_5$ was recovered (total ~1 gm). A third component of the mixture was not isolated.

Preparation of $ClSn[Co(CO)_4]_3$

Stannic chloride (2.6 gm, 10 mmole, 1.17 cc) in a slightly warmed THF solution was added to $Co_2(CO)_8$ (7.75 gm, 22.65 mmole) in THF. After stirring several hours at room temperature, the solvent was evaporated and the residue extracted several times with hot pentane. The pentane was evaporated to a purple solid. Recrystallization from pentane yielded 2.1 gms (31%) of deep red-purple needles, mp 95 - 98°.

Reduction of $ClSn[Co(CO)_4]_3$

Tris(tetracarbonylcobalt)tin chloride (500 mg, .75 mmole) was placed in ~ 50 cc degassed hexane. A solution of i-Bu_2AlH (1 cc, 1.04 N in heptane) was slowly added. After stirring 2 hours, the solvent was evaporated and the residue chromatographed on silica with benzene. Some decomposition was evident in solution. The eluant was filtered through celite and evaporated to reddish-black crystals, mp 158 - 160°, pure by TLC.

The product turned black upon drying in vacuo at 65°. After drying at 30° (100μ) there were no protons visible by nmr. Analysis--C: 17.91%, H: 0.97, Sn: 17.3, Co: 31.8. Calculated for the expected dimer $[Co(CO)_4]_3SnSn[Co(CO)_4]_3$; C: 22.8, H: 0.0, Sn: 18.8, Co: 28.0. The product remains unidentified at this time.

Identical results were achieved using one equivalent of reducing agent instead of an excess.

Proposed synthesis of (chlorodiphenyltin)manganese pentacarbonyl

$Ph_2Sn[Mn(CO)_5]_2$ (.221 gm, 1/3 mmole) and Ph_2SnCl_2 (.115 gm, 1/3 mmole) were dissolved in 10 cc THF and stirred. The products were analyzed by TLC in $CHCl_3$. After one day there was ~5% reaction, after 3 days 20%, and after one week about 80%.

When the same reactants were mixed dry and heated to ~140°C for 1-1/2 hours, there was very little reaction. In addition to the starting materials, there were two products present which appeared to be $Ph_2ClSnMn(CO)_5$ and $PhCl_2SnMn(CO)_5$.

Preparation of trimethylsiliconcobalt tetracarbonyl

Me_3SiH (2.67 gm, excess) was condensed onto resublimed $Co_2(CO)_8$ (1.2 gm). The mixture was heated to room temperature and stirred 10 minutes. After flushing the flask with argon, a residual grey powder (1.55 gm) remained. Sublimation at 30°, 200μ yielded 1.1 gms product (65%).

$Me_3SiCo(CO)_4$ and $Cl_2Sn[Co(CO)_4]_2$

$Me_3SiCo(CO)_4$ (.25 gm, 1 mmole) and $Cl_2Sn[Co(CO)_4]_2$ (.34 gm, 1 mmole) were mixed dry and heated at 100 - 110° C for 3 hours. The mixture was taken up in pentane, filtered, and the solvent evaporated. A purple solid was recovered, with some melting evident at 93 - 95° C, with a black residue remaining. In hexane the infrared spectrum showed $^{\nu}CO$ at 2086, 2079, 2067, 2048, 2040, ~2024 (two bands superimposed) and 2003 cm^{-1}. $ClSn[Co(CO)_4]_3$ exhibits $^{\nu}CO$ at 2088, 2049, 2043, and 2028 cm^{-1}.

Preparation of $Me_3SiFe(CO)_2Cp$

A solution of $Fe(CO)_2Cp^-$ (10 mmoles in THF) was added at room temperature to a THF solution of Me_3SiCl (1.7 gm, 15 mmole). After stirring 2 hours the solvent was evaporated, and the residue was extracted with hot pentane, filtered through celite and evaporated. The product was sublimed (50°, 100μ) to an orange waxy solid. Yield 1.6 gms (64%).

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IV. EXPERIMENTAL PROGRAM

NEW SUPERCONDUCTORS - Semi-Annual Report

Richard H. Bube and John W. McKenzie

$K_2Pt(CN)_4Cl_{0.3} \cdot x\ H_2O$

The results of some measurements of electrical conductivity and thermoelectric power on this material have been reported in the previous semi-annual report. A publication entitled, "Thermoelectric Analysis of Transport in Linear Transition Metal Organo-Metallic Compounds," by J.W.McKenzie, C. Wu and R.H.Bube appeared in Applied Physics Letters 21, 187 (1972). In addition to the previously reported results, studies here by D. Cahen showed that all of the water of hydration can be lost in a dehydration process but nothing else (e.g., not Cl_2), only about 70-80 percent of this water is restored by exposure to a humid atmosphere, Pauli paramagnetism is retained in the dehydrated state, and X-ray powder spectra indicate that dehydration results in a breakup of the crystal into small crystallites with a preferred orientation.

We attempted to measure the temperature dependence as a function of temperature of the electrical conductivity of dehydrated $K_2Pt(CN)_4Cl_{0.3}$ for comparison with the published variation for the hydrated compound and its Br analogue. Results of three such attempts are shown in Figure 1, together with published data on the hydrated $K_2Pt(CN)_4Br_{0.3} \cdot x\ H_2O$. Problems of reproducibility and hysteresis are evident. The data obtained over the widest temperature range, however, indicates a curvature with temperature variation the reverse of that found for the hydrated material. The curvature for the hydrated material is removed by changing from a $1/T$ to a $1/T^{1/2}$ plot, consistent with an interpretation in terms of a hopping process. Such is clearly not the case for the dehydrated material, which shows apparent activation energies between 0.1 and 0.2 eV.on a $1/T$ plot. That the conductivity process is quite different in the dehydrated material is indicated also by the change in sign of the thermoelectric power from positive to negative upon dehydration.

$Ir(CO_3)Cl$

Our previous measurements on $Ir(CO_3)Br$ indicated a positive thermoelectric power which could be interpreted as giving a temperature-independent hole density and a thermally activated hole mobility. In order to extend measurements on this material, we attempted to grow larger single crystals. The crystals are currently grown from $IrCl_3$ by vapor transport in CO at a temperature of about 170°C. Although a major increase in size appears unlikely, we hope to be able to make somewhat longer crystals. We also intend to investigate the properties of thin films made by sublimation of $Ir(CO_3)Cl$ in order to determine the degree of correlation of electrical, thermoelectric and optical properties measured on thin sublimed films with those same properties measured on single crystals.

$Ir(CO_2)$Acac

For another test of the effect of measurements on various different forms of the same material, we are investigating the electrical, thermoelectric and optical properties of $Ir(CO_2)$Acac in single crystal, pressed pellet and sublimed thin film form.

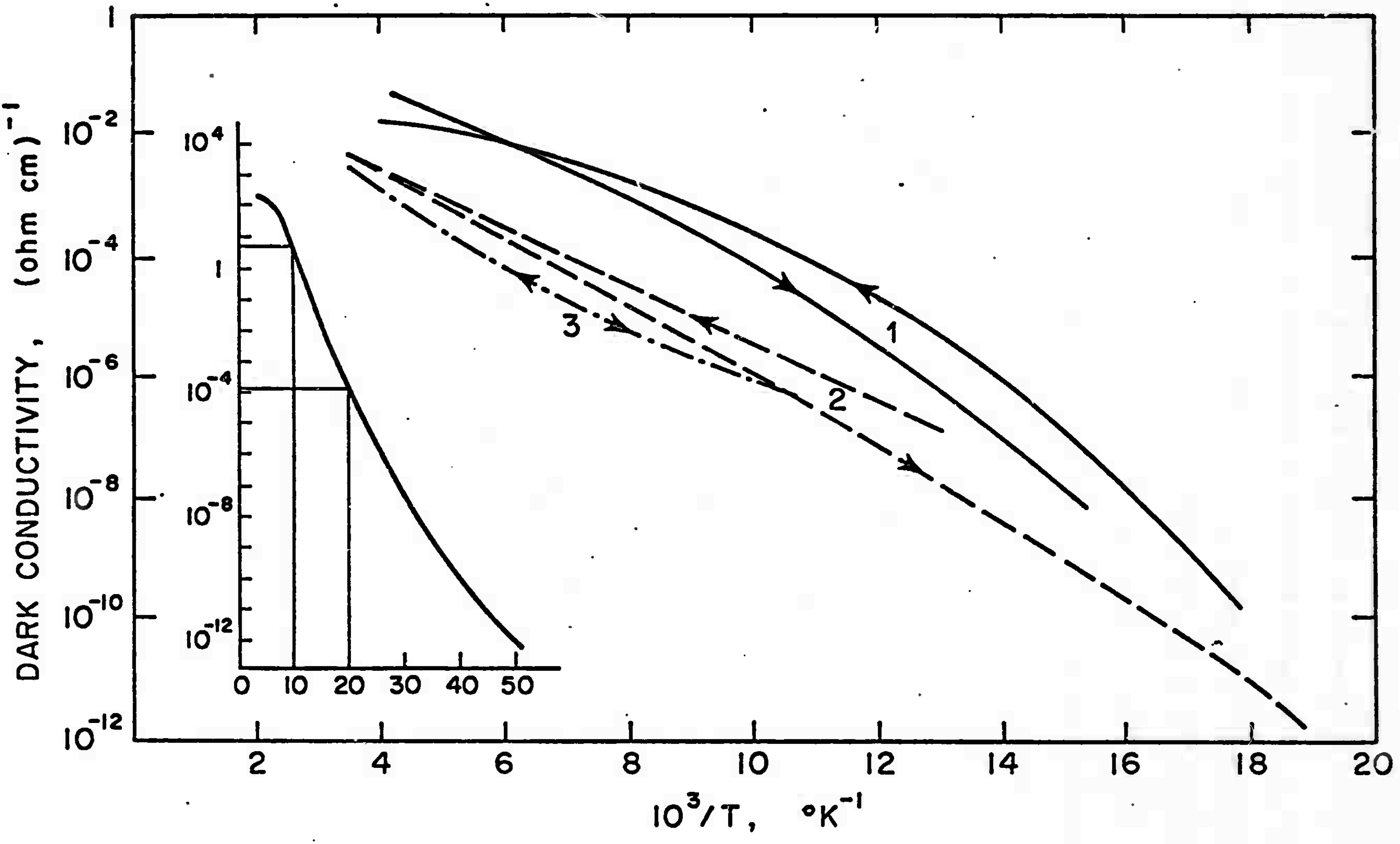


Figure 1. Dark conductivity of dehydrated $K_2Pt(CN)_4Cl_{0.3} \cdot x\ H_2O$ as a function of temperature. Curve 1: increasing and decreasing temperature with 4-point measurement; curve 2: increasing and decreasing temperature with 2-point measurement; curve 3: increasing and decreasing temperature with 4-point measurement. Inset shows for comparison the temperature dependence of the dark conductivity of $K_2Pt(CN)_4Br_{0.3} \cdot x\ H_2O$ in the hydrated state after D.Kuse and H.R.Zeller, Phys.Rev.Letters 27, 1060 (1971).

Thin Film Reflectance Measurements on Stacked d^8 Complexes

M. R. MacLaury and G. Wrighton

Introduction

Materials that contain linear chains of metal atoms have received a great deal of attention since the 1950's. These materials have been investigated via electrical conductivity and spectral (absorption and reflection) measurements. Compounds whose optical properties have been studied include: nickel bisdimethyl glyoxime ($Ni(dmg)_2$), platinum bisdimethyl glyoxime ($Pt(dmg)_2$),[1] Magnus Green Salt (MGS)($Pt(NH_3)_4PtCl_4$),[2] tetracyanoplatinates ($MgPt(CN)_4 \cdot 7H_2O$, $CaPt(CN)_4 \cdot 5H_2O$, $BaPt(CN)_4 \cdot 4H_2O$),[3] and a series of nickel and pallidium vic-dioximes.[4] An article by P. Day[5] in 1969 reviews all of the early work on spectral studies of these compounds. B. G. Anex[6] enumerates the many sources of error that one must consider in the interpretation of spectral data. Anex cites examples from some of the above sources where an incomplete understanding of spectroscopy or faulty experimental procedure yields incorrect conclusions.

The intense low energy absorption observed in the single crystal but not in the solution absorbance spectra of $Ni(dmg)_2$ was interpreted as caused by Ni-Ni bonds.[1] Futher support for Ni-Ni bonds was provided by Rundle,[7] who estimated that the Ni-Ni chains contributed about 10kcal/mole to the stability of the crystal. Rundle based his estimate on the relative solubilities of $Ni(dmg)_2$ (very insoluble) and $Cu(dmg)_2$ (very soluble). However an extensive study of the solubility of nickel and palladium vic-dioximes by Banks and Barnum[8] showed there to be no correlation between metal-metal "bond" lengths and molar solubility.

Molecular orbital calculations[9] of $Ni(dmg)_2$ show no evidence for bonding between nickel atoms in the ground state. A detailed study by Anex and Krist,[10] critical of previous work, suggests that Ni-Ni interactions in $Ni(dmg)_2$ are not necessary to account for the solid state absorption and reflection spectra. Anex and Krist assert that there is nothing unusual about bands polarized perpendicular to the molecular plane if the molecular orbitals have other than p_z symmetry. Previous workers[1,2,4] have used polarization results to infer metal-metal interaction. The low energy absorption band is assigned by Anex and Krist to a $d_{z^2} \rightarrow \text{ligand}\pi^*$ $1e^-$ excitations that is also seen in the free molecule spectrum. The lowering of this band is due to electrostatic crystal perturbations. Electrostatic and crystal packing forces may also account for the low solubility and column-stacking of $Ni(dmg)_2$. Both the molecular orbital calculations and the optical properties suggest that no Ni-Ni interactions take place in the ground state but there may be significant orbital overlap in the excited state. Recent work[11] on $Ni(dmg)_2$ indicates the existence of a band in the far UV at 53kK (189nM, 6.55eV). This band is assigned to a Ni-Ni charge transfer transition. All other lower energy bands are assigned to metal-ligand charge transfer and metal-metal or ligand-ligand local excitations.

Although spectral evidence shows no metallic or low energy gap absorption and thus no strong metal-metal interaction, high pressure experiments can be done to look for changes due to changing the metal-metal distance.[12] When single crystals of Magnus Green Salt and $Ir(CO)_2$(acetyl acetonate) are put under pressure up to 170kbar the metal-metal distance is decreased 8-10%. Not only does the electrical conductivity increase but at least one of the optical absorption bands is lowered. When the pressure is increased above 100kbar the conductivity levels off and then decreases. Also the energy of the absorption band is raised. These latter effects are probably due to intra molecular effects as the metal-ligand distances shorten. Molecular orbital calculations[13] were made on MGS in an attempt to interpret the pressure experiment the Pt-Pt ground state bond order was estimated to be 0.039 with a bond energy of about 0.2kcal/mole, too low to affect either chemical or physical properties. The calculations then assumed the Pt-Pt distance to change from 3.25Å to 2.80Å. At 2.80Å the Pt-Pt bond order is estimated to be 0.139. This, presumably, is enough to account for the increased electrical conductivity.

Structural Dependence of Reflectance Data

It is apparent that optical properties are difficult to interpret. One must do very careful work to assign the bands observed. However, it is hoped that simple thin film reflectance measurements can be used as a tool to determine whether or not one has a column stacked material. The results presented here give some hope that there is at least an empirical relationship between the intermetallic interactions in stacked d^8 complexes and their reflectance spectra.

Sample Preparation

Samples can be prepared for reflectance measurements in a number of ways. The best procedure would be to use single crystals, but these are difficult to grow in our case.

Samples can also be mixed with a support medium such as KBr and pressed into a pellet. The pure material can also be pressed into a pellet. The method we have choosen is to sublime a thin film onto a glass slide. This method has the advantage of using a small quantity of material (10-20mg) and one can obtain better reflecting surfaces than by the pressed pellet technique. The disadvantages of thin film reflectance is the random orientation of crystals, the lose of reflection due to transmission through the sample, and the dependence of the reflectance on film thickness.

Results and Discussion

The chemical structure of the materials studied provides an obvious method of classifying the results. Table 1 lists the compounds studied, grouped by compound type as well as the qualitative features of the reflectance spectra. A strong reflectance peak appears in some of these samples and in all of these cases strong absorption is observed at the reflection peak. See Figure 1 for typical results.

These results suggested a possible correlation between the reflection peak and the metal-metal separation in compounds which are known to be stacked in the solid state. As noted previously assignment of this band is not easy and to ascribe it to a metal-metal $d_{z^2} \rightarrow p_z$ band seems risky.[14] However, we feel justified in using this technique as a tool to compare a series of compounds looking for such a relationship.

The experimental data supports this idea. For example I-a shows a prominent reflectance peak at a low onset energy (1.35eV) and this material is known to have a short Ir-Ir distance (3.20Å).[15] The reflectance data for I-a can be compared with compound IV-b, which does not exhibit a peak. The crystal structure of IV-b has not been determined but the bulky size of R and R" should force the Ir-atom apart. Compounds with small R and R" show strong reflectance at low onset energies. Compounds I-a, b and c show higher onset energies as R and R" vary from CH_3 to CF_3 to CH_2CH_3. That is, as the R and R" group get bigger the onset energy gets greater.

The crystal structure[15] of VI-a shows that the Ir atoms do not stack in a linear chain but rather form a zig-zag chain with a Ir-Ir separation of 3.6Å and an interplane separation of 3.48Å. This compound exhibits a very weak reflection peak at 1.8eV. The structure of V-a is being determined by x-ray diffraction and preliminary results show Ir chains with an Ir-Ir separation of 3.38Å. This compound has a strong reflection peak starting at 1.2eV.

Compound VII, $Ir(CO)_3Cl$, shows somewhat different optical properties. First, its transmission is low in the near infrared, and second its reflectivity in the same region is high compared to the other compounds examined. It has only a very weak reflection peak despite a very short Ir-Ir separation of 2.78Å. Preparation and measurement of the reflection properties of $K_2(Pt(CN)_4)Br_{0.3}\cdot 2.3H_2O$ by pressed pellet yields a high reflection spectrum in the near infrared with no peak.

These observations suggest that $Ir(CO)_3Cl$ and $K_2(Pt(CN)_4)Br_{0.3}\cdot 2.3H_2O$ are similar species. The current literature suggests that $K_2(Pt(CN)_4)Br_{0.3}\cdot 2.3H_2O$ may be a one dimensional metal,[16] a one dimensional broken metallic chain system[17] or a semiconductor with a low energy gap.[18]

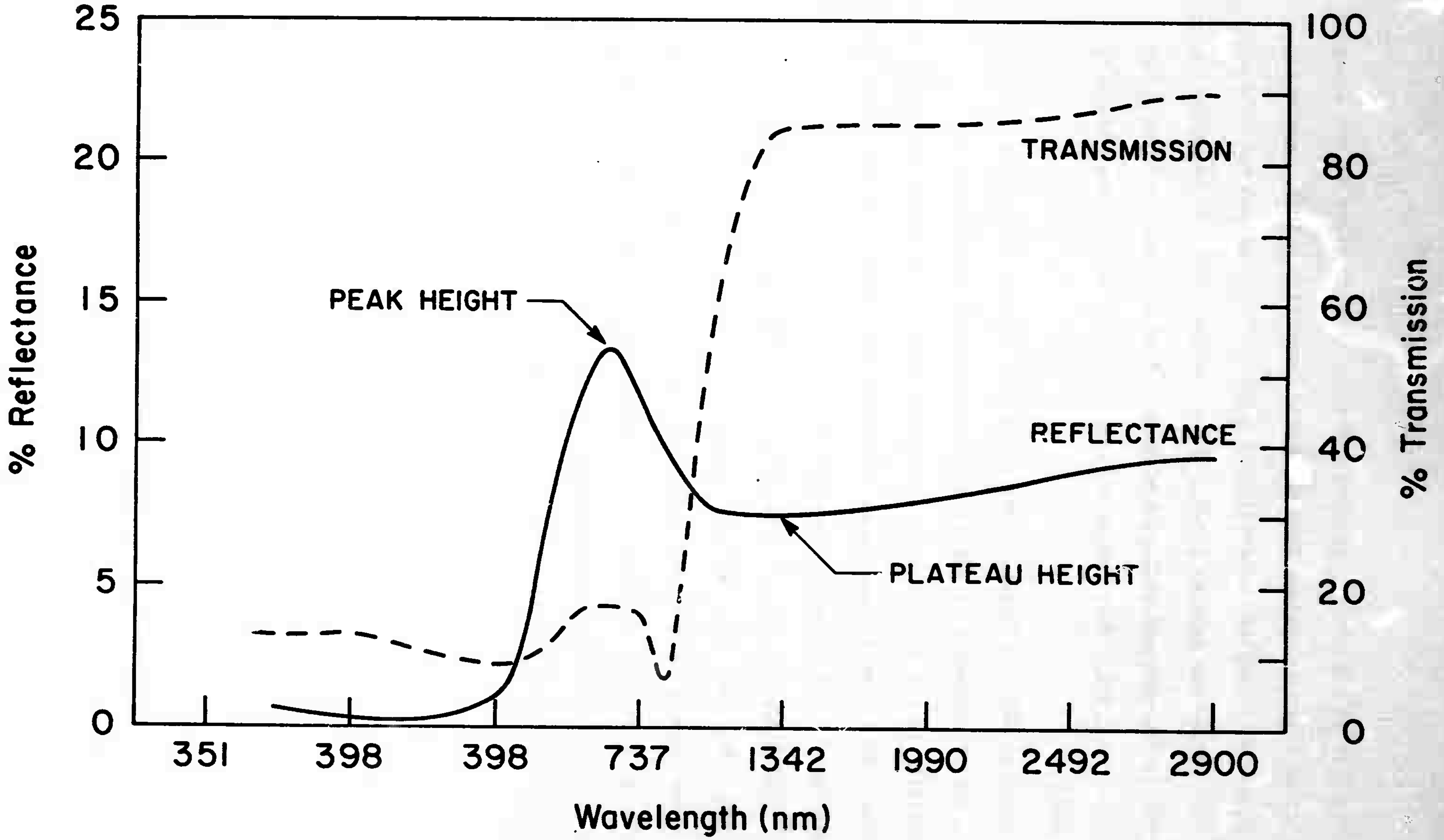
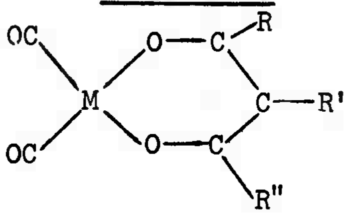

% Reflectance
25
20
15
10
5
0
% Transmission
100
80
60
40
20
0
PEAK HEIGHT
TRANSMISSION
REFLECTANCE
PLATEAU HEIGHT
351
398
398
737
1342
1990
2492
2900
Wavelength (nm)

Figure 1

Table 1

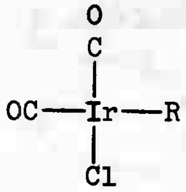
Reflectance



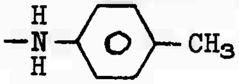
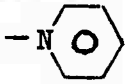
		M	R	R'	R"	Reflectance peak (eV)				M-M(Å)
						onset	fullwidth	peak	strength[+]	
I.	strong single peak									
	a)	Ir	CH_3	H	CH_3	1.35	1.10	1.9	1.75	3.20 chain
	b)	Ir	CF_3	H	CF_3	1.55	1.60	2.4	2.00	
	c)	Ir	CH_3CH_2	H	CH_3CH_2	1.65	1.60	2.2	1.69	
	d)	Rh	CH_3	H	CH_3	1.80	1.45	2.4	1.45	3.27 chain
	e)	Rh	CH_3	H	CF_3	2.2	1.1	2.7	1.47	
II.	weak single peak									
	a)	Ir	C_6H_5	H	C_6H_5	1.25	2.05	2.5	1.09	4
	b)	Ir	CH_3	CH_3	CH_3	1.45	1.4	2.3	1.15	dimer 3.29
III.	strong peak with other features									
	a)	Ir	CH_3	H	O-CH_2CH_3	1.8	1.0	2.1	1.35	
IV.	very weak or no peak									
	a)	Ir	CH_3	H	1-Azulene	-	-	-	-	
	b)	Ir	CH_2-$CH(CH_3)_2$	H	$CH_2CH(CH_3)_2$	-	-	-	-	

[+] Strength is calculated to be peak height divided by plateau height (See Fig. 1)

Table 1 (continued)



$\mathrm{OC{-}Ir(CO)(Cl){-}R}$

	R	Reflectance peak (eV)				M-M(Å)
		onset	fullwidth	peak	strength	
V.	strong single peak					
a)		1.2	1.1	1.7	2.5	3.38 chain
VI.	weak single peak					
a)	 (pressed pellet)	1.8	1.1	2.3	1.12	3.6 zig zag
VII.	high reflectance weak peak					
a)	CO (pressed pellet)	possibly mixed valence (metallic)				2.78 chain

Experimental

All preparations were carried out in these laboratories: using standard procedures which are described in another section of this report.*

The reflectance and transmission spectra were recorded on a Beckman DK-2A spectrometer over a wavelength range from 360nM (27.8kK, 3.45eV) to 2900nM (3.45kK, 0.43eV). A reflectance device was built by G. Wrighton to fit into the sample compartment of the spectrometer. The angle of incidence was not normal but about 48°. Two aluminum mirrors were used, the first to reflect the beam from the source onto the sample and the second to direct the reflected beam from the sample into the detector. The mirrors and sample were adjusted for each sample to give a maximum reflectance at 2900nM.

The sublimation apparatus was all glass with a ring seal joint. The condensing finger was open and could be cooled to -78°C with a dry ice/acetone slush. A glass cover slide (12mm diameter) was cleaned and fixed to the condensing finger with a small amount of petroleum jelly. The compound to be sublimed was placed in the bottom of the apparatus (10-50mg) and the apparatus evacuated (10^{-2}-10^{-5} torr). The condensing finger was then cooled to -78°C. Depending upon the compound the temperature of sublimation varied from room temperature (25°C) to 190°C. After visually determining that a good mirror surface had condensed, the sublimator was allowed to come to room temperature, then disassembled and the glass slide removed. The sample prepared in this manner was easy to handle and mount on the reflectance device. Transmission measurements were made through the glass.

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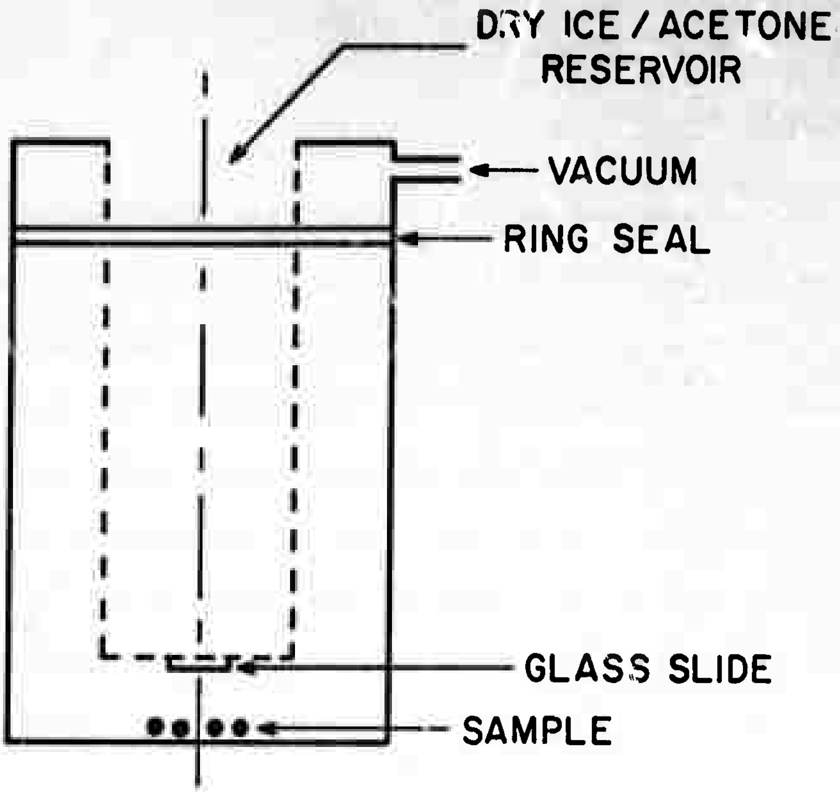
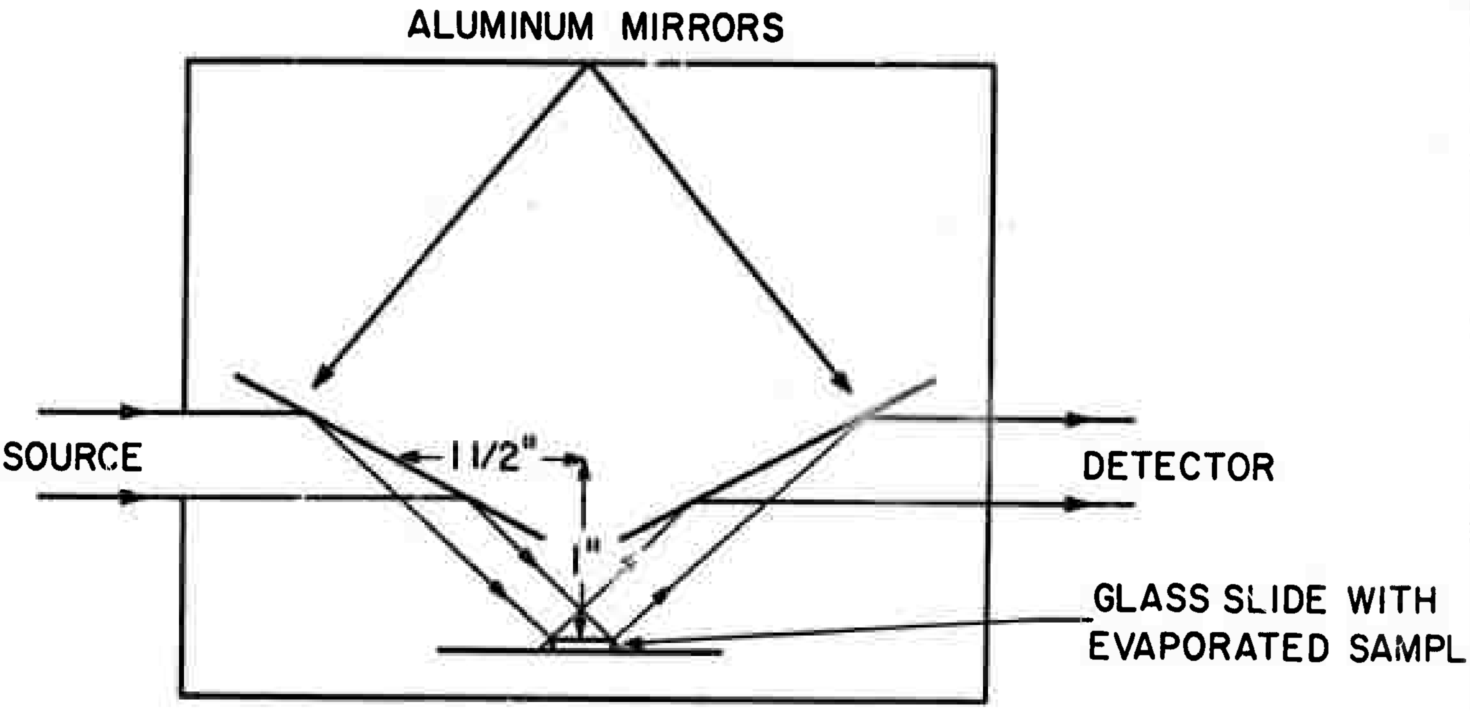
* M. R. MacLaury, this report.



SUBLIMATOR



REFLECTANCE DEVICE

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LOW TEMPERATURE SPECIFIC HEAT OF ONE-DIMENSIONAL $K_2Pt(CN)_4Cl_{0.3} \cdot n(H_2O)$

by

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ABSTRACT: The low temperature specific heat of one-dimensional $K_2Pt(CN)_4Cl_{0.3} \cdot n(H_2O)$ is reported. Within experimental accuracy the linear temperature contribution to the specific heat is zero. This result is consistent with both the variable range and interrupted strand hopping models.

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RJ 1092 (#17927)
September 13, 1972
Solid State Physics

Recently, there has been considerable experimental and theoretical interest in crystalline solids which exhibit one-dimensional (1-D) properties.[1-5] In particular the "mixed-valence" square planar compounds of platinum and iridium have attracted attention because of their large 1-D conductivity (1-100 $\text{ohm}^{-1}\text{cm}^{-1}$ at room temperature) and their possible use as a base structure for a higher temperature superconductor.[6] In these compounds the planar complexes stack to form linear chains of metal atoms, the chains being insulated from each other by the organic side groups. The metal atom is partially oxidized and in the band picture the overlapping d_{z^2} orbitals of the metal atoms form a partially filled 1-D band.

Two very similar models have been proposed to explain the properties of these 1-D compounds.[7] One model, first discussed by Bloch, Weisman and Varma,[2] is based on X-ray crystallographic data which shows that structural disorder exists along the 1-D chain and in such a system it is known that all the electronic states are localized. The electronic properties result from electrons hopping between localized states near the Fermi level. The other model, originally based on the "metallic" optical reflectivity observed by Kuse and Zeller[8] and Geserich et al,[9] treats the system as a series of co-linear metallic strands each of which is interrupted by an insulating lattice defect. Rice[10] has recently pointed out that the presence of the random potential along the strands is not necessarily inconsistent with the existence of a one-dimensional metallic state. Both models claim to explain the dc and ac conductivity, the magnetic susceptibility and the optical properties.

In this letter we report the first measurements of the specific heat of a typical 1-D square planar complex $K_2Pt(CN)_4Cl_{0.3}\cdot n(H_2O)$. Our measurements place a definite upper limit on the length of any metallic strands and place an upper bound on the apparent density of states at the Fermi surface. Our results are consistent with either of the above two models but they do not distinguish between them.

The specific heat was measured between 1.5 and 6.5°K using a relaxation time method specifically designed for small samples.[11] Because of thermal time constant effects it was not possible to measure the heat capacity over a wider temperature range. The sample consisted of several single crystals (total mass 27 mg) greased to a silicon thermometer. The addenda contributed approximately 10% to the total heat capacity over the temperature range measured. To insure that the sample composition did not change during evacuation of the sample chamber the sample was cooled rapidly to 77°K in a helium atmosphere before evacuation. The crystals had a bright coppery appearance before and immediately after the experiment. The result obtained for the heat capacity of $K_2Pt(CN)_4Cl_{0.3}\cdot n(H_2O)$ is shown in Fig. 1. A least squares fit of the data to the relation $C = \gamma T + \beta T^3 + \delta T^5$ gave the parameters

$$\gamma = 0\pm 0.51 \times 10^{-4}\ \mathrm{j/mole\text{-}^\circ K^2}$$

$$\beta = 2.45\pm 0.10 \times 10^{-3}\ \mathrm{j/mole\text{-}^\circ K^4}$$

$$\delta = 1.45\pm 0.07 \times 10^{-5}\ \mathrm{j/mole\text{-}^\circ K^6}$$

where the errors are discussed below. In order to check the accuracy of the temperature scale, the addenda corrections and to get a reliable estimate of systematic and random errors, a high purity germanium sample of similar heat capacity to the Pt-salt was measured from 1.5 to 4.2°K. We measured a Debye Temperature $\theta_D = 366\pm 4$°K (accepted value 374±4°K) and $\gamma = 0\pm 1.0 \times 10^{-6}$ j/mole-°K^2. Since we expect no electronic contribution to the specific heat ... germanium we have taken the error in γ (in $j/°K^2$) as a measure of our maximum possible error (systematic and random) in the linear contribution to the heat capacity for our apparatus. This error, when put on a molar basis, gives us an upper limit on γ, for $K_2Pt(CN)_4Cl_{0.3}\cdot n(H_2O)$, of 0.51×10^{-4} $j/mole\text{-}°K^2$. Using the standard expression $\gamma = (\pi^2/3)k_B^2N(0)$ for the coefficient of the linear term in C for a Fermi system, we find an upper limit for the density of states at the Fermi surface, $N(0) \leq 7.6 \times 10^{+19}$ states $cm^{-3}eV^{-1}$. We can compare this result with some estimate of the expected value of N(0) based on the two proposed models.

One estimate of N(0) can be obtained from the number of holes in the valence band and a measure of the width of the conduction band, essentially treating the system as a metal (interrupted strand model). The sharp cutoff of the reflectivity above 2 eV observed by Kuse and Zeller[8] and Geserich et al[9] suggests that the width of the band is ≥2 eV. On the other hand, for free electrons the total width of a band from $k = 0$ to $k = \pi/a$ where a is the Pt-Pt distance, would be about 4.6 eV. A reasonable estimate of the bandwidth would thus be ≈2-5 eV. The hole density can be obtained from the number of Cl atoms incorporated in the lattice. Assuming each Br atom acts an acceptor, introducing one hole in the Pt valence band, then the number of holes/unit volume will be 1.05×10^{21} holes/cm^3. Using the above estimate of the bandwidth and assuming a constant density of states across the band, we find $N(0) \approx 2\text{-}5 \times 10^{20}$ states $cm^{-3}eV^{-1}$.

On the other hand, a somewhat broader band and thus a reduced value of N(0) might result from the contribution of the random potential at the Pt sites. The simplest model of the variable range hopping mechanism[2] gives a conductivity

$$\sigma = \sigma_o \exp -\left(\frac{T_o}{T}\right)^{1/2} \quad (1)$$

where $T_o = 4\alpha/\rho k_B$, ρ is the number of states per unit length per unit energy, and α^{-1} is the mean decay length of the wave function of the localized state. The conductivity data[4,8,12] yield a value of $T_o \approx 5.8 \times 10^4$ K, while $\rho \approx 0.02\text{-}0.05$ states eV-Å assuming the above bandwidth and hole density. From the expression for T_o we find $\alpha^{-1} \approx 16\text{-}40$Å. This is much larger than the interatomic spacing $a = 2.89$Å which thus indicates that the states are weakly localized.

To understand this result we have examined the properties of the eigenstates and eigenvectors of the single particle Hamiltonian for electrons in a one-dimensional chain. We use the tight binding approximation with a nonzero resonance integral β only between neighboring sites and include a contribution from a random potential (with standard deviation σ) at each atomic site. We find that if $\sigma << |\beta|$ then $a\alpha << 1$ and the states are weakly localized. Moreover, in this case the width of the band is essentially determined by $|\beta|$ with a trivial contribution from the random potential. This condition appears to hold for our material in which, as shown above, $a\alpha \approx 0.18 - 0.07$. If we had assumed that the width of the band was broadened beyond 5 eV by a strong random potential ρ would be decreased and hence $a\alpha$ would have to decrease to give the same T_o. This would imply weaker localization contradicting our assumption of a strong random potential. If we had assumed a band width less than 2 eV, ρ and hence $a\alpha$ would be larger, however, the reflectivity data appears to rule out this possibility.

Thus we see that by either model we expect $N(0) \approx 2\text{-}5 \times 10^{20}$ states $\text{cm}^{-3}\text{eV}^{-1}$, which is considerably larger than that found by our specific heat measurement.

The previous arguments have assumed that the electronic system comes to equilibrium within the time required to measure a data point (~100 sec). However, in a system of localized states the transfer of energy by hopping becomes very improbable at low temperatures[13] and this assumption must be examined with care. The reasoning which leads to (1) is based on a hopping probability given by

$$\Gamma \approx \nu \exp -\left(\frac{T_o}{T}\right)^{1/2}$$

where $\nu \approx 10^{12}$ sec^{-1} is a typical phonon frequency. With $T_o = 5.8 \times 10^4$°K we see that the above condition for equilibrium in the experiment is violated below about 56°K and, in fact, if we take the model seriously, in the helium range the time for equilibrium to be reached would be in excess of 10^{39} secs. The reason for this is that the mean distance between sites whose energies lie within kT of one another at these low temperatures is so large that hopping between them is extremely improbable. The apparent absence of a linear term in the specific heat could then be due to the slow response of the system and would be consistent with the hopping model.

The result is also consistent with the interrupted strand model but does impose a weak limit on the strand length. The separation of the electronic levels in a one dimensional chain of length L is given by $\Delta(L) = \pi h v_f/L$, where the Fermi velocity v_f is $\approx 10^8$ cm/sec. If $\Delta(L)$ is larger than kT (10^{-3} eV at 10°K) the electronic specific heat will result from a distribution of Schottky anomalies and we expect no linear term in T. Our results require that $L < 2 \times 10^{-4}$ cm, since strand lengths greater than this would produce a measurable linear term in the specific heat. On the other hand if interchain hopping can occur so that equilibrium between the chains can be established, then instead of the Schottky anomalies we will again obtain a contribution to the specific heat linear in T and a finite density of states at the Fermi level. However, the situation here is essentially the same as for the localized state model and we expect this hopping probability to be negligibly small at low temperatures.

Thus our results can be understood on the basis of either model but a distinction between the two cannot be made from the specific heat results alone. We suggest that the apparent absence of a linear term in T is a consequence of the long relaxation time. It does not necessarily imply an insulating or semiconducting state with N(0) = 0. If this suggestion is valid one would expect hysteresis in the thermal properties of these compounds at higher temperatures.

Our results show no evidence for one or two dimensional lattice modes. These would cause the specific heat to fall below the curve $C = \beta T^3$. From our measured value of β we find a Debye Temperature $\theta_D = 246°K$ assuming 19 atoms per molecule. As shown in Fig. 1 above $\sim 3.3°K$ the specific heat is, in fact, larger than the value given by βT^3. This could be evidence for a breakdown of the Debye approximation or a Schottky contribution from a metallic strand length distribution. A further contribution to the specific heat would result from low energy optical phonons caused by the weak coupling between the Cl^- ion, K^+ ion, water molecules and the $Pt(CN)_4^{--}$ complex. Such a contribution has been observed in low temperatures specific heat measurements in other quasi one- and two-dimensional systems such as CdI_2[14] and Rb_xWO_3.[15] We plan to extend our measurements to higher temperatures to clarify this effect.

In summary, our specific heat measurement on $K_2Pt(CN)_4Cl_{0.3} \cdot n(H_2O)$ shows no evidence of a linear term in the specific heat at low temperatures. We suggest that this result may be a consequence of the inordinately long thermal relaxation time of the electronic system rather than the absence of states at the Fermi surface. These long relaxation times are characteristic of systems in which hopping dominates the transport properties and should apply to both the variable range hopping and interrupted strand hopping models.

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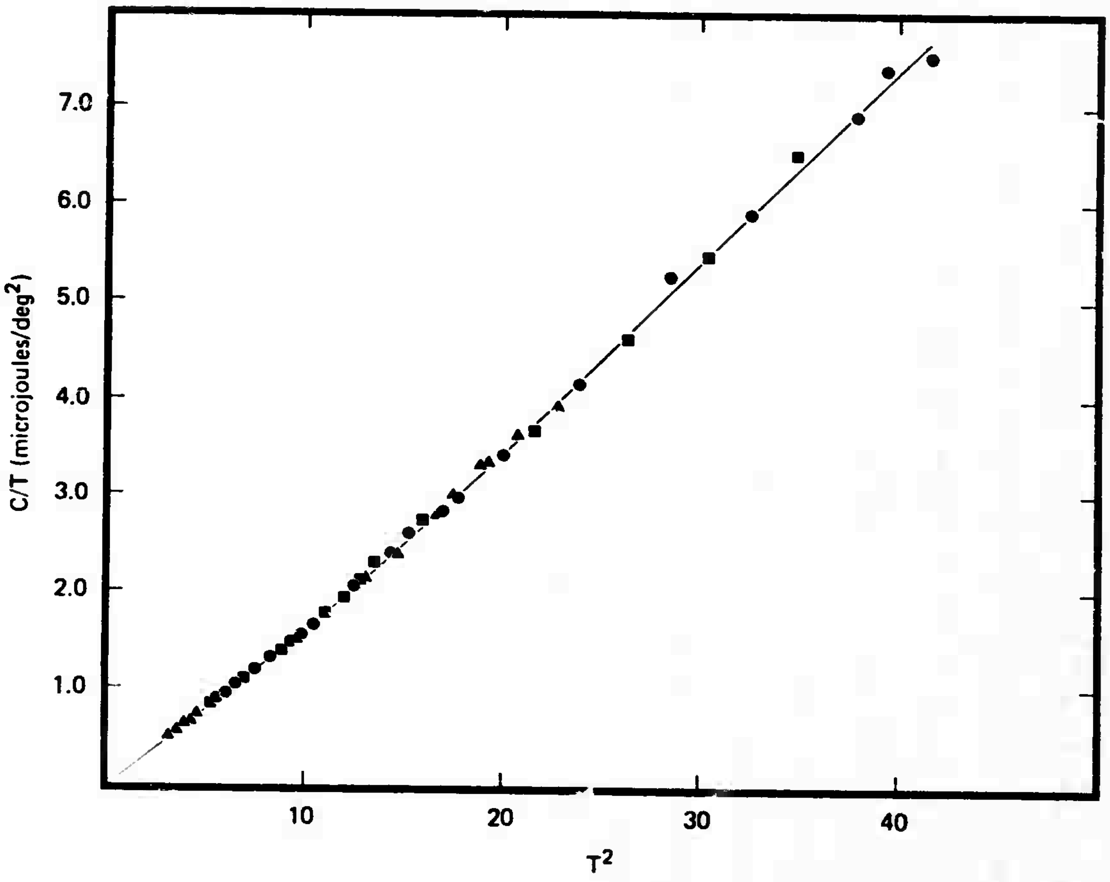

Figure 1. Heat capacity of $K_2Pt(CN)_4Cl_{0.3} \cdot n(H_2O)$ plotted as C/T vs. T^2 between 1.5 and 6.5° K. Corrections have been made for the approximately 10% addenda. The total sample mass was 27 mg (6.2×10^{-5} moles). The squares, circles and triangles are data from three different runs.

List of Publications

1. "Dynamic Effective Electron-Electron Interaction in the Vicinity of a Polarizable Molecule," W. A. Little and H. Gutfreund, Phys. Rev. B4, 817 (1971).
2. "Concept of Generalized Chladni Forces: Application to an Electron-Optical Light Pipe," W. A. Little, J. Appl. Phys. 43, 2901 (1972).
3. "Thermoelectric Analysis of Transport in Linear Transition-Metal Organometallic Compounds," John W. McKenzie, Chen-ho Wu, and Richard H. Bube, Appl. Phys. Lett. 21, 187 (1972).
4. "Low Temperature Specific Heat of One-Dimensional $K_2Pt(CN)_4Cl_{0.3}\cdot n(H_2O)$," R. L. Greene and W. A. Little, Phys. Rev. Letters 29, 718 (1972).
5. "Thomas-Fermi Screening in One Dimension," D. Davis, Phys. Rev. B, to be published.
6. "Molecular Modeling by Computer," Proc. IBM Res. Symp. on Computational Methods for Large Molecules and Localized States in Solids, to be published.
7. "Iridium (I) and Platinum (II) Complexes with Cyanine Dye Base Ligands," T. Winkler and C. Mayer, submitted for publication.

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