+2 ml Eisessig; b) Cu^{2+}: 100 ml Tetrahydrofuran + 0,5 ml konz. HCl. – Nachweis: a): Na^+ 1,5proz. Lösung von Violursäure in H_2O; b) Cu^{2+}: verd. NH_3 und 0,1proz. Lösung von Rubeanwasserstoffsäure in Alkohol.

Wir danken dem *Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung* für die Unterstützung dieser Arbeit.

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231. Iridium (I) and Platinum (II) Complexes with Cyanine Dye Base Ligands[1]

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(18. 7. 72)

Summary. The preparation of cyanine dyes by coordination of cyanine dye bases with transition metals is described. The significance of these complexes for the realization of an excitonic high temperature superconductor is discussed.

Introduction. – We are concerned with the design and the preparation of possible high temperature superconductors built according to *Little*'s theory [1], which requires a one dimensional conductor, the so-called spine, to which polarizable groups are attached. The polarizable groups have to exhibit a very intense ($\log\varepsilon \approx 5$) and narrow absorption in the visible or near infrared [1]. Systems with such characteristics are cyanine dyes, squarylium dyes and azulenium dyes. *Little* proposed a long (> 100 Å) polyene as the spine. Due to the considerable synthetic difficulties and the expected low stability of the dye substituted polyenes, *Collman* [2] proposed later to form the spine by an intermetallic chain. The metal atoms of such a chain may either be covalently bonded to one another or simply associated in the solid state through crystal packing forces [2]. Planar d^8 complexes of second and third row transition metals such as $[Pt(NH_3)_4][PtCl_4]$ [3], $Pt(dmg)_2$ [4] and *cis*-$[Ir(acac)(CO)_2]$ [5] are often stacked in the crystalline state resulting in metallic chains. Such substances have been found to be highly anisotropic semiconductors [5]. However, it has also been suggested [6] that impurities may play a certain role in determining the unusual conductivity of these complexes. Partial oxidation of such planar complexes sometimes results in non-stoichiometric compounds, which consist of more strongly associated intermetallic chains as evidenced by shorter intermetallic distance (≈ 2.85 Å as compared with 3.25 Å for second and third row d^8 complexes [7]). An example is $K_2[Pt(CN)_4]Br_{0.3} \cdot nH_2O$. Such partially oxidized complexes exhibit higher conduc-

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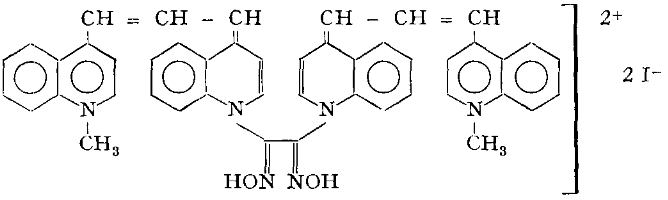
tivities [8] than the simple d^8 complexes. The electron transport properties of the former are thought to arise from hopping of charge carriers between essentially metallic regions [9]. We have studied methods for introducing dye groups, primarily of the cyanine dye type, into such intermetallic chains. One approach is to synthesize ligands, such as the glyoxime **1**, which contain dye substituents [10]. In this paper, we describe another method – coordination of a cyanine dye base directly to the transition metal.



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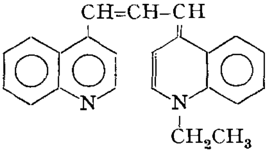
Results and discussion. – Three cyanine dye bases (bases of which cyanine dyes are the quaternary salts) **2**, **3** and **4** have been transformed into the iridium (I) and platinum (II) complexes listed in the Table. The cyanine dye base **2** was prepared by thermal dequaternization of cryptocyanine using a high boiling tertiary amine (N,N-diethylaniline) following the procedure of *Gevaert Photo Producten* NV [11], the cyanine dye base **3** and **4** by treating 4-picoline with 4-(β-anilinovinyl)-quinoline methiodide or 4-methylpyrimidine with 4-(β-anilinovinyl)-quinoline ethiodide in the presence of KOH. Experiments according to the method of *Barent* & *Kendall* [12], which uses pyridine or an excess of the heterocyclic base instead of KOH, gave only traces of **3** and **4**. The cyanine dye bases were characterized by their mass, NMR. (exp. section) and electronic spectra (Table). Protonation of cyanine dye base **2** (λ_{max} 527 nm, 95% ethanol) with HCl in 95% ethanol afforded a typical cyanine spectrum (λ_{max} 700 nm), essentially the same as cryptocyanine (λ_{max} 705 nm, 95% ethanol), which is a quaternary salt of **2**.



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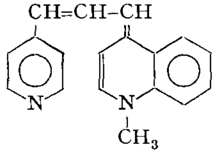

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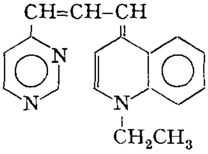

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Iridium complexes of **2**, **3** and **4** (**5**, **6** and **7**, respectively, Table) were prepared by treating each cyanine dye base with $IrCl(CO)_3$ [13] [14]. Upon complexation, the chromophor exhibits a bathochromic shift of about 80 nm (Table) with bands broader than those of the parent dye (e.g. cryptocyanine in the case of **5**). A similar, but larger bathochromic shift occurs on protonation or quaternization of these cyanine dye bases, indicating that the iridium is coordinating to the base through the σ-electron pair on the nitrogen of the aromatic ring rather than through any of the π-electrons, and that a cyanine dye is formed upon complexation. The pyrimidine complex **7** exhibits two equal maxima, one at 576 nm and the other one at 617 nm. This pattern is undoubtedly due to the presence of the second nitrogen, since 4,4'-diphenyl-1,1'-dimethyl quinazocarbocyanine iodide [15] also exhibits two equal bands. Steric arguments suggest coordination at the 1 rather than the 3 position. Simple analogues of the iridium dye base complexes were prepared by treating $IrCl(CO)_3$ with pyridine [16] and 4-methylquinoline, furnishing complexes **8** and **9**. The elemental analysis and the presence of two ν_{CO} bands (2060 and 1980 cm^{-1} in KBr disks) for the complexes **5** to **9** are consistent with the formulation *cis*-$[IrCl(CO)_2(B)]$ (where B is the heterocyclic base). Composition and *cis* configuration of *cis*-$[IrCl(CO)_2$(pyridine)] (**8**) have been confirmed by X-ray diffraction analysis [17].

The square planar platinum (II) complex **10** was obtained by treating $K[PtCl_3(DMSO)]$ with cyanine dye base **2** in aqueous ethanol. Recrystallization from acetone afforded violet crystals with a golden luster. The NMR. spectrum of **10** confirmed the presence of the two ligands, DMSO and cyanine dye base **2**. A *trans* configuration is assigned to **10** in analogy with similar complexes derived from reaction of $K[PtCl_3(DMSO)]$ with simpler amines [18] and results from the strong *trans* effect of DMSO [19]. The bathochromic shift of 80 nm upon coordinating platinum (II) with the cyanine dye base **2** is similar to the shift observed with iridium (I).

Crystals of all complexes prepared fail to show evidence of intermetallic interaction, with their conductivities ($\sigma_{25°} \leq 10^{-12}$ ohm^{-1} cm^{-1}, pressed pellet, two probe[2])) in the range of organic insulators. In the case of *cis*-$[IrCl(CO)_2$(pyridine)] (**8**), X-ray diffraction analysis [17] demonstrates the presence of an iridium chain with a metal separation of 3.62 Å. However, the iridium atoms are arranged in a zig-zag chain preventing significant overlap of the p_z or d_{z^2} orbitals on adjacent iridium atoms. The absence of this overlap would give a much reduced conductivity. Complexes **5**, **9** and **10**, having a quinoline nucleus directly attached to the metal atom, very likely do not

Optical data

Compound		λ_{max} a) b)	$\log\varepsilon_{max}$ a) b)
2	4-[3-(1-ethyl-4(1*H*)-quinolylidene)-propenyl]-quinoline	499 509 c)	4.57 4.62 c)
3	4-[3-(1-methyl-4(1*H*)-quinolylidene)-propenyl]-pyridine	476	4.55
4	4-[3-(1-ethyl-4(1*H*)-quinolylidene)-propenyl]-pyrimidine	506	4.57
5	*cis*-$[IrCl(CO)_2(B)]$ B = **2**	583	4.64
6	*cis*-$[IrCl(CO)_2(B)]$ B = **3**	542	4.58
7	*cis*-$[IrCl(CO)_2(B)]$ B = **4**	576 617	4.75 4.75
10	*trans*-$[PtCl_2(DMSO)(B)]$ B = **2**	578 600 c)	 4.69 c)

a) Only bands in the visible region are listed. b) In benzene. c) In acetone.

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[2]) We are indebted to *G. Wrighton* for the conductivity measurements.

form intermetallic chains at all upon crystallization. In these complexes, the plane of the quinoline nucleus should be rotated out of the coordination plane due to interaction of the H(8) with a neighboring ligand, precluding effective solid state stacking of the square planar complexes and formation of intermetallic chains. The coordination geometry of the complexes **6** and **7** should not interfere with stacking in the crystalline state, but there are two reasons for the possible absence of intermetallic chains. First, these complexes are mainly cyanine dyes, so that the strong attractive forces between the chromophoric groups undoubtedly dominate the crystal packing forces, which may lead to a solid state structure without intermetallic chains. Second, the presence of such a chain would require a crystal structure with rather large empty space, which is an energetically unfavorable arrangement.

In summary, the novel cyanine dyes can be formed by coordination of a cyanine dye base with a transition metal. These complexes are potential model compounds to test the concept of the proposed high temperature superconductor, but further work is needed to find ways to favor the formation of the intermetallic chains necessary for conduction.

Experimental Part

General Information. Microanalyses were performed by Messrs. *E. Meier* and *J. Consul*, Stanford Microanalysis Laboratory. The electronic spectra were obtained with *Beckman* DK2A spectrometer, the IR. spectra with a *Perkin Elmer* 457 grating spectrometer and the NMR. spectra with a *Varian* T-60 (MHz) spectrometer. The mass spectra (*Atlas* CH4 and *AEI* MS9, 70 eV) are presented as *m/e* (relative intensity). All melting points are uncorrected.

4-[3-(1-ethyl-4(1H)-quinolylidene)-propenyl]-quinoline (**2**). A mixture of 3.5 g cryptocyanine [20] and 500 ml N, N-diethyl-aniline was stirred and refluxed for $2^1/_4$ hours under protection from light. During this time, N_2 was passed through the mixture and 300 ml solvent was distilled off. The other 200 ml solvent was removed by steam distillation and the residue extracted with benzene. The benzene solution was dried (Na_2SO_4) and the solvent removed under vacuum. Recrystallization from a few ml acetone yielded 1.25 g (51%) blue black crystals, m.p. 161°; MS.: 324 (100, M^+), 293 (12), 196 (24), 184 (15), 167 (10), 148 (11), 143 (11). NMR.: (DMSO-d_6) δ 6.4–8.7 (*m*, 15), 3.90 (*q*, 2), 1.24 (*t*, 3).

4-[3-(1-methyl-4(1H)-quinolylidene)-propenyl]-pyridine (**3**). A mixture of 150 mg 4-(β-anilinovinyl)-quinoline methiodide [21], 15 ml dry 4-picoline and 300 mg KOH was 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 (Na_2SO_4) and the solvents removed under vacuum. Recrystallization from benzene/hexane furnished 85 mg (85%) red needles, m.p. 143°; MS.: 261 (19), 260 (100, M^+), 259 (72), 258 (12), 244 (10), 243 (8), 182 (23), 181 (10). NMR.: (acetone-d_6) δ 6.1–8.4 (*m*, 13), 3.42 (*s*, 3).

4-[3-(1-ethyl-4(1H)-quinolylidene)-propenyl]-pyrimidine (**4**). A mixture of 503 mg 4-(β-anilinovinyl)-quinoline ethiodide [21], 3.7 g 4-methylpyrimidine and 3 g KOH was heated at a bath temperature of 135° for 70 min. The resulting mixture was extracted with methanol. The extract was diluted with benzene and extracted with water until the water layer was colorless. The solvent was removed and the residue chromatographed on alumina (*Merck*) with benzene/pyridine 5:1. Recrystallization from benzene/hexane gave 120 mg (35%) violet needles, m.p. 114°; MS.: 275 (38, M^+), 196 (26), 195 (100), 167 (10), 166 (16), 157 (16). NMR.: (DMSO-d_6) δ 6.1–9.2 (*m*, 12), 3.60 (*q*, 2), 1.24 (*t*, 3).

Preparation of the iridium complexes **5**, **6**, **7**, **8** *and* **9**. Equimolar amounts of $IrCl(CO)_3$ [13] and the appropriate base (**2**, **3**, **4**, pyridine or 4-methylquinoline, respectively) were refluxed in dry benzene for $1^1/_2$ hours. The hot benzene solution was filtered and the filtrate concentrated, whereby the complex precipitated. Recrystallization from benzene/hexane yielded about 80% of the appropriate complex. *cis*-$[IrCl(CO)_2(pyridine)]$ (**8**) has already been prepared [16].

cis-[*IrCl(CO)*$_2$*(4-[3-(1-ethyl-4(1*H*)-quinolylidene)-propenyl]-quinoline)*] (**5**). Dark, hairlike needles, steelblue luster, m.p. 165° (dec.).

$C_{25}H_{20}ClIrN_2O_2$	Calc.	C 49.38	H 3.32	Cl 5.83	Ir 31.61	N 4.61
(608.10)	Found	,, 49.55	,, 3.39	,, 5.80	,, 31.38	,, 4.35

cis-[*IrCl(CO)*$_2$*(4-[3-(1-methyl-4(1*H*)-quinolylidene)-propenyl]-pyridine)*] (**6**). Dark, hairlike needles, steelblue luster, m.p. 170° (dec.).

$C_{20}H_{16}ClIrN_2O_2$	Calc.	C 44.16	H 2.96	Ir 35.33	N 5.15
(544.01)	Found	,, 44.32	,, 2.99	,, 35.03	,, 5.23

cis-[*IrCl(CO)*$_2$*(4-[3-(1-ethyl-4(1*H*)-quinolylidene)-propenyl]-pyrimidine)*] (**7**). Blue black needles, blue luster, m.p. 153° (dec.).

$C_{20}H_{17}ClIrN_3O_2$	Calc.	C 42.97	H 3.07	Cl 6.34	Ir 34.38	N 7.52
(599.03)	Found	,, 42.94	,, 3.28	,, 6.70	,, 34.80	,, 7.34

cis-[*IrCl(CO)*$_2$*(4-methylquinoline)*] (**9**). Bright yellow needles, m.p. 125°.

$C_{12}H_9ClIrNO_2$	Calc.	C 33.77	H 2.13	Cl 8.31	Ir 45.03	N 3.28
(426.86)	Found	,, 33.96	,, 2.21	,, 8.46	,, 44.64	,, 3.33

trans-[*PtCl*$_2$*(dimethylsulfoxide)(4-[3-(1-ethyl-4(1*H*)-quinolylidene)-propenyl]-quinoline)*] (**10**). A mixture of 106 mg **2**, dissolved in 200 ml 70% ethanol, and 130 mg $K[PtCl_3(DMSO)]$ [19] was stirred for eight 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 160 mg (73%) violet crystals with golden luster. A compound indistinguishable from **10** by microanalysis and IR. in $CHCl_3$ can be obtained by mixing $[PtCl_2(DMSO)_2]$ and **2** in DMSO and distilling off the solvent. NMR.: (DMSO-d_6) δ 6.6–9.5 (*m*, 15), 4.08 (*q*, 2), 2.50 (*s*, 6), 1.28 (*t*, 3).

$C_{25}H_{26}Cl_2N_2OPtS$	Calc.	C 44.91	H 3.92	Cl 10.61	N 4.19	Pt 29.18	S 4.80
(668.56)	Found	,, 45.13	,, 3.91	,, 10.69	,, 4.37	,, 29.03	,, 4.98

We are indebted to Professor *J. P. Collman* and Professor *W. A. Little*, of the Departments of Chemistry and Physics, Stanford University, respectively, for many helpful discussions and the reading of the manuscript. We wish to thank *M. MacLaury* for preparing a sample of $IrCl(CO)_3$.

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232. The Reaction of Norbornene with Lead Tetraacetate and Thallium Trinitrate

Preliminary Communication

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(24. V. 72)

Summary. The reaction of norbornene with lead tetraacetate is found to be much more complex than previously reported. In acetic acid and in benzene, the *syn*-7-norbornenyl, 3-nortricyclyl, and *syn* and *anti*-7-acetoxy-*exo*-2-norbornyl acetates were characterized. In methanol, the isolated products represented most of those expected from the competition of methanol and acetate in the neutralization of the intermediate carbocations. The reaction of norbornene with thallium trinitrate in the above solvents yielded very complex mixtures besides the above mentioned products which were formed in about 50% yield.

The reaction of norbornene (**1**) with lead tetraacetate (LTA) was first described by *Alder, Flock & Wirtz* [1]. In acetic acid, they isolated only *exo*-2-*syn*-7-diacetoxynorbornane (**4**) in 85% yield. In benzene, they reported **4** (59%), 3-acetoxynortricyclane (**3**, 26%) and one unspecified isomer of 7-acetoxynorbornene (5%). In methanol, finally, they reported *exo*-2-*syn*-7-dimethoxynorbornane (**7**, 43%), 3-methoxynortricyclane (**6**, 4%) and *exo*-2-acetoxy-*syn*-7-methoxynorbornane (**9**, 30%). These results have not been questioned, except in their mechanistic interpretation [2]. The above procedure may even have been utilized for providing an 'authentic' sample of **7** needed in the structure determination of a rearrangement product of 2-chloro-2,3-epoxy-norbornene [3]¹).

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¹) In this work the authors reached stereochemical conclusions by comparing one transformation product with **7**. It is nor clear whether they used a sample prepared according to [1], as stated in their text, or according to [4] as indicated in their experimental. Regardless, they found their diacetate **4** to be contaminated by **5** and by another minor product (which we also observed), and it is therefore most likely that their sample of **7** was also contaminated with **8**. This is further suggested by their NMR. spectrum, which resembles that of a mixture of **7** and **8** near 3.5 ppm.