

the toluidine fractions collected by gas chromatography. Results from the competitive aminations are summarized in Table IV.

Isomerization Studies.—The catalyst (0.2 mole) was added to a cold solution of the amine (0.1 mole) in the aromatic compound (1 mole). The mixture was heated under nitrogen to the highest temperature for the corresponding amination reaction and maintained at that temperature for at least the longest heating period of the amination reaction. After the mixture was cooled and poured into hydrochloric acid-ice, the amine was isolated by the usual method (88–95% recovery). In no case was any isomerization indicated by infrared analysis.

Preparation of Methyl Azide.—The method was adapted from the procedure of Dimroth and Wislicenus.³⁴ Dimethyl sulfate (170 ml., 1.8 moles) was added to an aqueous solution of sodium azide (39 g., 0.6 mole) at 70–80° with intermittent addition of 3 *N* sodium hydroxide in order to keep the reaction mixture slightly alkaline. The methyl azide was passed in the gas phase through a tube packed with soda-lime and sodium hydroxide pellets (to remove any hydrazoic acid contaminant) and was collected in a trap cooled with Dry Ice-acetone. The product (31 g., 91%) was used without further purification.

In a modified procedure, the sodium azide was dissolved in a buffer solution containing sodium bicarbonate and sodium carbonate in a 1:1 molar ratio. Dimethyl sulfate was added to the solution at 70–80°, and the product was collected as described. Although better control of the pH of the reaction mixture was

(34) O. Dimroth and W. Wislicenus, *Ber.*, **38**, 1573 (1905); O. Dimroth, *ibid.*, **39**, 3905 (1906).

maintained by this procedure, the yield of product was lower (51–64%). On the basis of qualitative tests³⁵ with aqueous ferric chloride and ethanolic silver nitrate, the product did not appear to be contaminated with hydrazoic acid.

Methyl Azide-Toluene-Aluminum Chloride.—After the addition of methyl azide, and then aluminum chloride, to toluene at –5°, the mixture was heated to the reaction temperature. The basic product was isolated by the standard method. Table VI summarizes the results.

Analytical Procedures.—The isomer distributions of the toluidines and chloroanilines were determined in cyclohexane by a modified base line procedure³⁶ with a Beckman IR-7 or IR-8 infrared spectrophotometer. The absorbance was measured at the following characteristic wave lengths (μ): *ortho* (toluidine, 13.42; chloroaniline, 13.50); *meta* (toluidine, 13.02; chloroaniline, 13.07); *para* (toluidine, 12.36; chloroaniline, 12.23).

Analyses of the aniline-toluidine mixtures were performed with an F and M Model 500 gas chromatograph: 12 ft. by 0.25 in. column, 14% Apiezon L on Chromosorb P-5% sodium hydroxide³⁷; helium flow rate, 55 ml./min.; column temp., 175°.

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(35) P. A. S. Smith, *J. Am. Chem. Soc.*, **70**, 320 (1948).

(36) R. L. Bohon, R. Isaac, H. Hoftiezer, and R. J. Zellner, *Anal. Chem.*, **30**, 245 (1958).

(37) The caustic was used in order to minimize tailing of the peaks; see J. J. Cincotta and R. Feinland, *ibid.*, **34**, 774 (1962).

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Organometallic Semiconductors. I. Derivatives of Oximes of 1,5-Diacyl-2,6-dihydroxynaphthalenes¹

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The problem of preparing semiconducting polymers is discussed. It is pointed out that the best hope of obtaining technically useful materials of this kind lies in the field of coordination polymers. A series of new polymers of this type are described which show interesting electrical properties; these are metal derivatives of the dioximes of 1,5-diformyl- and 1,5-diacetyl-2,6-dihydroxynaphthalene.

Introduction

Electronic engineering has been revolutionized in the past 15 years by the introduction of a host of new devices based on semiconductors. The further development of this field has, however, been hampered by the limited number of suitable materials. All those in current use are metalloids (*e.g.*, germanium), alloys (*e.g.*, indium antimonide), or simple inorganic compounds (*e.g.*, cadmium oxide); the number of possible combinations of this kind is very limited. The situation could be transformed if suitable organic semiconductors could be found; it would then be possible to prepare ranges of materials with controlled properties, since organic molecules by their nature offer wide scope for structural variation.

Attempts to develop suitable organic semiconductors have, however, proved disappointing.^{3,4} A number of

materials have been prepared which act as semiconductors and in which the energy gaps between the filled and conduction bands lie in the required range; however, the carrier mobilities in them have been much too small—orders of magnitude less than in typical inorganic semiconductors such as germanium or silicon.

The reasons for this are well understood. In the first place organic compounds form molecular crystals, the forces between adjacent molecules being relatively weak; there is consequently little electronic coupling between adjacent molecules and electrons find it difficult to jump from one molecule to another. Secondly, many of these materials have been amorphous polymers; the lack of ordered structure in such a material has the effect of scattering electrons when they try to flow through it and so lowers the conductivity.

The first difficulty can be minimized by using very large molecules, so as to reduce the number of gaps between one molecule and another. It is of course essential that electrons be able to migrate freely about each individual molecule; this can be achieved if the molecule is completely conjugated, the π -electrons occupying π -MO's that cover the whole system.

Completely conjugated organic polymers are known: for example, the poly-*p*-phenyls. However, such compounds are not easy to prepare, and their physical

(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF 62-104. A preliminary account of part of it has appeared: M. J. S. Dewar and A. M. Talati, *J. Am. Chem. Soc.*, **85**, 1874 (1963).

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(3) For reviews see D. D. Eley and M. R. Willis, and H. Akamatu and H. Inokuchi in "Symposium on Electrical Conductivity in Organic Solids," H. Kallmann and M. Silver, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, pp. 257, 277.

(4) H. A. Pohl and H. A. Pohl, J. A. Bornmann, and W. Itoh in "Organic Semiconductors," J. J. Brophy and J. W. Buttrey, Ed., The Macmillan Co., New York, N. Y., 1962, pp. 134, 142.

properties are very unsatisfactory; they are obtained as infusible, insoluble, amorphous powders. Not only does this make it impossible to fabricate them into suitable shapes, but it also reduces their carrier mobilities for the second reason indicated above.

It occurred to us that all these difficulties might be avoided by making suitable coordination polymers of transition metals. If the ligands are aromatic and can each bind two metal atoms, then through-conjugation becomes possible, the metal atoms using their valence shell d -orbitals to form $d\pi:p\pi$ bonds to the adjacent ligands. Polymers of this kind should be easily obtained and they offer two further intriguing advantages.

The first of these rests on the fact that metal-ligand bonds are formed reversibly; it should therefore be possible to crystallize polymers of this kind by heating them with a suitable solvent. The problem is just the same as that of crystallizing silica; in each case crystallization involves the breaking and reforming of bonds to convert a disordered structure to an ordered one. Such a process would be quite impossible in a normal organic polymer, but it should be possible in the case of a suitable coordination polymer. A crystalline polymer of this kind would be very likely to meet all our requirements.

The second possible advantage is based on a consideration of the types of metal most likely to form suitable polymers. For through-conjugation to be possible, each metal atom must form π -bonds to two adjacent ligands *using the same d -orbital*. This can clearly be achieved if the ligands are coplanar and occupy sites *trans* to one another in an octahedral or square planar complex. In other cases, *e.g.*, where the ligands are *cis* to one another, or are in a tetrahedral complex, through-conjugation is probably unimportant; in these cases the central atom seems to prefer to use different d -orbitals to form π -bonds to the different ligands, the use of a single d -orbital for this purpose being geometrically unfavorable.⁵

In order to ensure coplanarity, it is almost essential to use chelating ligands, and to arrange these about the metal in a square coplanar array. This has the further advantage of enabling the metal to use two d -orbitals for π -bonding; thus if the ligands lie in the xy plane, the d_{z^2} and d_{y^2} orbitals of the metal will be ideally placed to π -bond simultaneously to both ligands (Fig. 1). This in turn requires the metal to be either one forming square coplanar complexes (*e.g.*, Cu^{II} , Ni^{II}), or one forming octahedral complexes with two *trans* positions blocked by ligands of some other type. Clearly the former alternative is far preferable. Now complexes of this kind are often linked together by metal-metal bonds; nickel dimethylglyoxime provides a good example. Linkage of polymer molecules to each other by metal-metal bonds would of course be expected to increase greatly the ease of intermolecular migration of electrons and hence the carrier mobility.

Most of the coordination polymers that have been reported were prepared with the object of finding new thermostable materials rather than semiconductors. Most of the ligands used in these studies were consequently of "insulating" type, in which the conjugative path between the two adjacent metal atoms is interrupted by saturated groupings; in cases where the

(5) See M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).

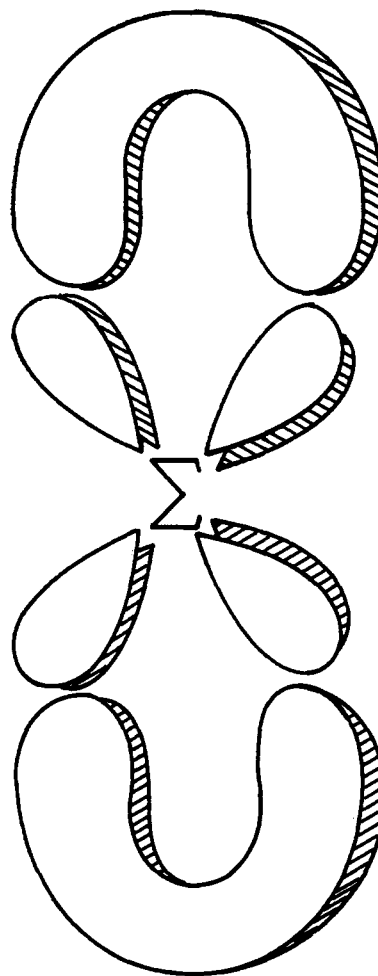


Fig. 1.—Diagram of orbitals in a square-planar complex formed by two conjugated chelating ligands.

ligands themselves were suitable (*e.g.*, rubeanic acid), unsuitable metals (*e.g.*, beryllium) were used. The only semiconducting polymers of this kind so far reported seem to be the cupric derivatives⁶ of 1,7-dihydroxyphenazine, 2,5-dihydroxy-*p*-benzoquinone, and rubeanic acid. The copper phthalocyanin polymers of Felmayer and Wolf⁷ and Epstein and Wildi⁸ were not true coordination polymers, but coordination complexes of organic polymers in which the molecules were held together by normal covalent bonds. The same was true in effect of the ferrocene ketone polymers of Pohl,⁴ since ferrocenes are not formed reversibly.

We became interested in this field through work on a related problem, the oxidation of aromatic systems by electron transfer. It occurred to us that coordination compounds of appropriate transition metals might act as catalysts in such reactions, and that polymeric materials of this kind might be particularly suitable. However, the electrical properties of the first two series of polymers we prepared have proved so interesting that we plan an extensive survey of such compounds.

Procedures and Results

For reasons indicated above, metals forming square-planar complexes are the most promising. The choice of suitable ligands is then dictated by three requirements. First, the ligand must be able to bind two metal

(6) S. Kanda and S. Kawaguchi, *J. Chem. Phys.*, **34**, 1070 (1961).

(7) W. Felmayer and I. Wolf, *J. Electrochem. Soc.*, **106**, 1141 (1958).

(8) A. Epstein and B. S. Wildi, *J. Chem. Phys.*, **32**, 324 (1960).

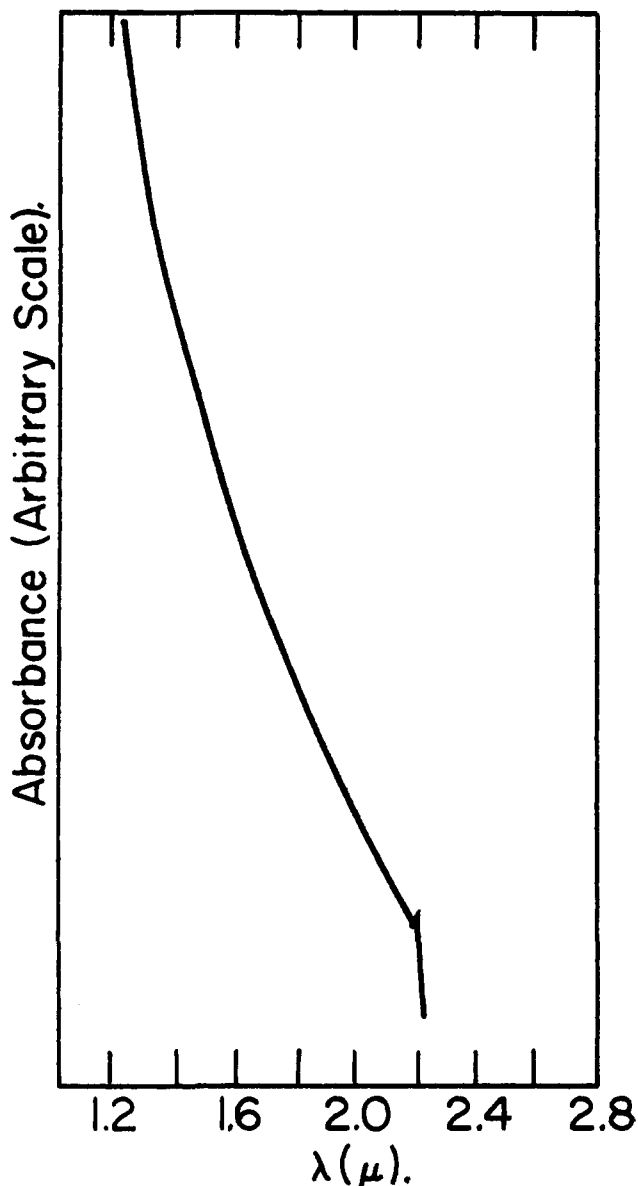


Fig. 2.—Infrared spectrum of the cupric derivative of IIb in a potassium iodide disk.

atoms by chelate linkages. Second, the chelating groups must be ones that combine strongly with the appropriate metals. Third, there must be a direct conjugative path from one metal to another in the complex. These conditions are easily met by using aromatic ligands, and by choosing chelating groups that are known from experience to combine well with square-planar metals.

Our preliminary work has been based on the fact that 2-hydroxy-1-naphthaldoxime (I) is a good analytical reagent for metals such as Cu^{II} , Ni^{II} , etc. We therefore set out to prepare the corresponding double ligand (IIa), the oxime of 1,5-diformyl-2,6-dihydroxynaphthalene (IIIa). This proved surprisingly difficult and success was achieved only after many attempts; IIIa was finally obtained in poor yield from 2,6-dihydroxynaphthalene by reaction with hexamethylenetetramine in acetic acid followed by hydrolysis. Since the synthesis of IIIa was so troublesome, we also made the dioxime (IIb) of the known⁹ diacetyldihydroxynaphthalene (IIIb); a preliminary account of

(9) I. F. Fieser and W. C. Lothrop, *J. Am. Chem. Soc.*, **57**, 1459 (1935).

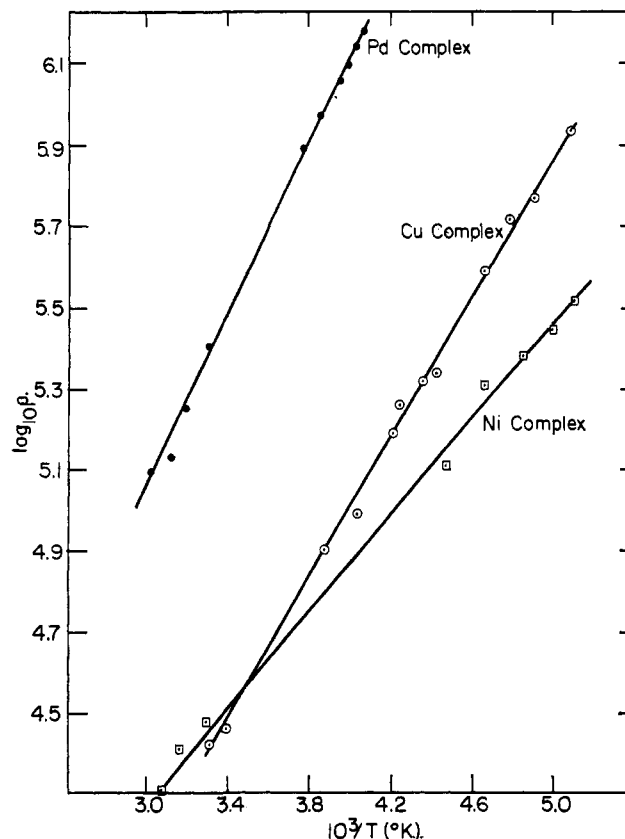
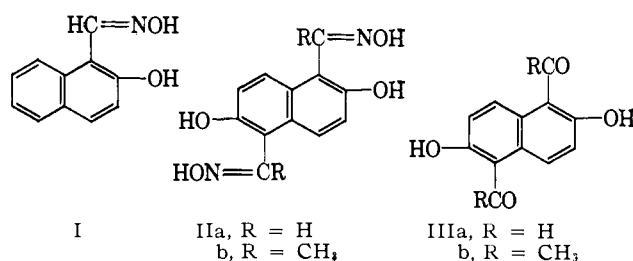


Fig. 3.—Temperature dependence of resistivity (ρ) for metal derivatives of IIa.

the preparation and properties of the copper complex of IIb has appeared.⁹



Copper(II), nickel(II), and palladium(II) derivatives of the dioxime II were prepared by the methods described below as dark-colored powders which decomposed without melting and were insoluble in organic solvents. The absorption spectra showed absorption edges in the near infrared, measured in potassium bromide or iodide disks. The absorption extended through the visible region. Figure 2 shows a typical spectrum, showing the absorption edge.

The electrical properties of the polymers were measured in disks, prepared at *ca.* 9×10^4 p.s.i., thickness *ca.* 1 mm., which were clamped between steel plates. The resistance was measured as a function of temperatures over the range -78 to $+78^\circ$, using a Keithley Model 515 megohm bridge for high resistances and a d.c. bridge method for low resistances.

The resistivity (ρ) of a semiconductor is given as a function of temperature by

$$\log \rho = \log \rho_0 + E_a/kT \quad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, ρ_0 is a constant which provides a measure

TABLE I
 SPECTROSCOPIC AND ELECTRICAL DATA FOR POLYMERS

Ligand	Metal	E_g , e.v.	ρ_0 , ohm cm.	ΔE , e.v.
IIa	Cu(II)	0.345	34.5	0.23
IIa	Ni(II)	.238	29.4	.23
IIa	Pd(II)	.418	82.2	.24
IIb	Cu(II)	.73	51.8	.56
IIb	Ni(II)	.668	92.0	.56
IIb	Pd(II)	1.13	17.4	.58

 TABLE II
 ANALYTICAL DATA FOR POLYMERS

Ligand	Solvent	Composition of polymer	Analyses, %							
			Calculated				Found			
			C	H	N	M	C	H	N	M
IIa	EtOH-NH ₃ -H ₂ O	(C ₁₂ H ₈ N ₂ O ₄) ₂ Cu ₃ (OH) ₂ ·8H ₂ O	33.6	4.0	6.5	22.2	32.6	3.3	7.6	22.7
IIa	EtOH-NH ₃ -H ₂ O	(C ₁₂ H ₈ N ₂ O ₄) ₁₀ Ni ₁₁ (OH) ₂ ·40H ₂ O	37.5	4.2	7.3	16.8	36.4	3.6	7.4	16.8
IIa	EtOH-NaOH-H ₂ O	(C ₁₂ H ₈ N ₂ O ₄) ₁₀ Pd ₁₁ (OH) ₂ ·16H ₂ O	36.6	2.9	7.1	29.8	37.0	3.2	7.2	30.9
IIb	MeOH-AcOH	(C ₁₄ H ₁₂ N ₂ O ₄)Cu	50.1	3.6	8.3	18.9	50.1	4.1	8.1	17.4
IIb	EtOH-NH ₃ -H ₂ O	(C ₁₄ H ₁₂ N ₂ O ₄)Ni·2H ₂ O	45.8	4.4	7.6	16.0	45.6	4.0	7.6	15.3
IIb	EtOH-NaOH-H ₂ O	(C ₁₄ H ₁₂ N ₂ O ₄)Pd·2H ₂ O	40.5	3.9	6.8	25.7	40.0	4.3	6.0	26.7

of the carrier mobility and E_a , the activation energy for conductance, is a measure of the gap E_g between the filled and conduction bands, where $E_g = 1/2E_a$.

Figure 3 shows a plot of $\log \rho$ vs. $1/T$ for the metal derivatives of IIa; the plots are linear as eq. 1 requires.

Table I shows values for ρ_0 and E_g for each of the six polymers prepared, together with the transition energies (ΔE) corresponding to onset of absorption in the infrared. The values of ΔE should again correspond to differences in energy between the filled and conduction bands; however, the observed value of E_g is likely to be somewhat greater than ΔE at normal temperatures since the upper levels of the filled band are partly depleted and the lower levels of the conduction band partly filled. This will reduce the absorption near the absorption edge and so make its onset indefinite.

Discussion

The polymers described above are interesting in three respects. First, their resistivities were quite low. Second, the carrier mobilities in them were quite high, the values for ρ_0 being much smaller than the majority of those reported⁴ for organic materials. Third, the continuous absorption to the high frequency side of the absorption edge implies that the energy levels of the individual molecules have fused into wide bands.

These are very encouraging conclusions, for the polymers described here are by no means ideal. In the first place their elemental analyses indicate that in most cases molecules of water were coordinated to the metal atoms, preventing the formation of possible metal-metal bonds; in the second place the compounds were certainly amorphous, and the resulting disorder would inevitably decrease the carrier mobilities.

There are also indications that the molecular weights of these compounds may not have been high. Thus while the products from IIb analyzed as 1:1 copolymers of metal and ligand, the Ni(II) and Pd(II) com-

plexes of IIa seemed to have degrees of polymerization of about ten only, while the corresponding cupric derivative seemed to have a still lower molecular weight. It is of course difficult to place much confidence on the results of analyses of such ill-defined materials, but the carbon-metal ratios at least do seem significant.

These results suggest that more suitable organo-metallic polymers may well prove of practical value as semiconductors; combined with the theoretical

reasoning given above, they also suggest that attempts to find useful semiconductors among other classes of organic compounds are probably doomed to failure.

It is unlikely that the polymers described in this paper will be obtained as single crystals, since the ligands involved are prone to hydrolysis. We are at present extending this work to polymers derived from more stable ligands, where the polymers might be converted to crystalline form by heating under pressure with water or dilute acids. Under these conditions hydrolysis and reformation of the metal ligand bonds could well lead to crystallization.

Experimental

Dioxime of 1,5-Diacetyl-2,6-dihydroxynaphthalene.—1,5-Diacetyl-2,6-dihydroxynaphthalene was prepared by the method of Fieser and Lothrop.⁹ The dioxime separated from aqueous alcohol in colorless crystals, m.p. 247–248°.

Anal. Calcd. for C₁₄H₁₄N₂O₄: C, 61.3; H, 5.1; N, 10.2. Found: C, 61.1; H, 5.2; N, 10.0.

1,5-Diformyl-2,6-dihydroxynaphthalene.—A solution of hexamethylenetetramine (15 g.) and 2,6-dihydroxynaphthalene (4 g.) in acetic acid (50 ml.) was boiled 4 hr. under reflux. Alcoholic hydrochloric acid (60 ml.) was then added and the mixture boiled for a further 4 hr. and then diluted with water and allowed to cool. Next day the 1,5-diformyl-2,6-dihydroxynaphthalene was collected and crystallized from benzene, forming reddish yellow rhombs, m.p. 277–278°.

Anal. Calcd. for C₁₂H₈O₄: C, 66.7; H, 3.7. Found: C, 66.8; H, 3.8.

Dioxime of 1,5-Diformyl-2,6-dihydroxynaphthalene.—The dioxime separated from ethanol in pale yellow crystals, m.p. >300°.

Anal. Calcd. for C₁₂H₁₀N₂O₄: N, 11.4. Found: N, 11.2.

Preparation of Metal Complexes.—The complexes were prepared by mixing equimolecular amounts of the metal salt (cupric acetate, nickel chloride, palladous chloride) and the dioxime, dissolved in a suitable solvent. The polymers separated as dark brown powders which were washed with alcohol and dried. They did not melt below 300° and were insoluble in all the usual solvents. Table II shows the solvents used and analytical data for the compounds. The third column gives the composition of the material corresponding to the calculated values.