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Phenazine Complexes. Their Preparation and Their Electrical Conductivity*

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The photo-reduction of phenazine was carried out in isopropyl alcohol in the presence of ferric chloride or stannic chloride. In the course of the photo-reduction, a metal chelate precipitated. The metal chelate was composed of unstable black needle crystals; it was presumed, from the results of the elementary analysis, the visible and the infrared absorption spectra and the ESR spectra, to be Fe^{2+}- or Sn^{2+}-chelate of *N*-monohydrophenazyl. On the other hand, the reduction of phenazine with stannous chloride and hydrochloric acid gave a phenazhydrin - stannic chloride-complex, which was more stable than the photo-reduction products. Their resistivities at 20°C had low values of from 10^5 to 10^8 ohm-cm.

The reduction of phenazine with stannous chloride and hydrochloric acid produces a complex containing stannic chloride; the structure of this complex is not yet known, however. When this complex is treated with an aqueous solution of sodium hydroxide, it loses stannic chloride and produces free phenazhydrin.[1] The irradiation of phenazine in isopropyl alcohol by ultraviolet light also produces phenazhydrin, together with acetone.[2] The intermediates of the photo-reduction to phenazhydrin from phenazine are not certain, but one of them is supposed to be the *N*-monohydrophenazyl radical. If the *N*-monohydrophenazyl radical is produced in this process and if an electron acceptor is also present in the system, the *N*-monohydrophenazyl radical may react with the electron acceptor to produce a complex. In order to verify this assumption, the photo-reduction of phenazine was carried out in isopropyl alcohol in the presence of ferric chloride or stannic chloride. As was expected, the complex of *N*-monohydrophenazyl with ferric chloride or stannic chloride was obtained as crystals of a plate form. These complexes have an electrical conductivity as organic semiconductors. In the

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[1] G. R. Clemo and H. McIlwain, *J. Chem. Soc.*, **1934**, 1991.

[2] C. Dufraisse, A. Etienne and E. Toromanoff, *Bull. Soc. Chim. France*, **1953**, 140; G. A. Swan and D. G. I. Felton, "Phenazines," Interscience Publishers, New York (1957), p. 48.

Table I. The value of spin concentrations, ρ_{20} and $\Delta\varepsilon$ of metal chelates

Compound	g-Value	Half width gauss	Spin concn. spins/mol.	ρ_{20} ohm-cm.	$\Delta\varepsilon$ eV.
ph-phH$_2$	2.0033	7.1	3.8×10^{21}	3.7×10^{10}	1.32
(ph-phH$_2$)$_2$ SnCl$_4$	2.0033	6.2	3.1×10^{23}	1.6×10^{5}	0.75
phH·SnCl$_2$	2.0033	1.0	3.9×10^{23}	6.0×10^{8}	1.19
phH·FeCl$_2$	2.032	440	2.0×10^{22}	6.4×10^{7}	1.06

present paper we will report on the syntheses of these complexes and on their properties as organic semiconductors. In addition, the properties of the phenazhydrin - stannic chloride-complex will be investigated.

Experimental

Materials.—Phenazine was prepared according to the methods described in the literature[3]; it was purified by repeated recrystallizations from ethanol.

The Preparation of Metal Chelates.—*Reduction with Stannous Chloride and Hydrochloric Acid.*—To a solution of 0.54 g. of phenazine in 20 ml. of ethanol there was added at room temperature a solution of 0.56 g. of anhydrous stannous chloride in 10 ml. of ethanol. No crystals precipitated from the greenish reaction mixture. However, the acidification of the reaction mixture with 1—2 ml. of concentrated hydrochloric acid immediately gave black-green needle crystals. After the above acidified mixture had been further refluxed for five minutes, the hot mixture was filtered and left to cool. After the cooled filtrate had then been filtered out, 0.56 g. of the metal chelate was obtained as black-green needle crystals; this was then recrystallized from ethanol.

Found: N, 11.40; Cl, 14.33. Calcd. for $C_{48}H_{36}N_8$-SnCl$_4$: N, 11.42; Cl, 14.46%.

The metal chelate decomposed to phenazine and stannic chloride when dissolved in ethanol. Therefore, the phenazine content in the metal chelate could be estimated from the optical densities of the ultraviolet and visible absorption spectra of phenazine at 250 mμ and 370 mμ in ethanol. The results showed the molar ratio of phenazine to stannic chloride to be 4 : 1.

The Photo-reduction of Phenazine with Isopropyl Alcohol.—*In the Presence of Stannic Chloride.*——A solution of 0.41 g. of phenazine and 0.69 g. of stannic chloride in 40 ml. of isopropyl alcohol was placed in a test tube of a vycol (30 mm. in inner diameter, 0.5 mm. in wall thickness) and irradiated under an atmosphere of nitrogen at room temperature for 30 hr. with a 100W. mercury lamp placed 5 cm. from the vessel. About 0.32 g. of black prism crystals were precipitated. The crystals collected by filtration were dried over phosphorus pentoxide under the reduced pressure of 2—5 mmHg.

Found: N, 7.43; Cl, 19.40. Calcd. for $C_{12}H_9N_2$-SnCl$_2$: N, 7.57; Cl, 19.20%.

From the results of the visible absorption spectra, the molar ratio of phenazine to stannous chloride in the product was estimated to be 1 : 1.

In the Presence of Anhydrous Ferric Chloride.—A solution of 0.12 g. of phenazine and 0.17 g. of anhydrous ferric chloride in 25 ml. of isopropyl alcohol was irradiated for 7 hr. in a manner similar to that described above. About 0.1 g. of black needle crystals were thus precipitated. The crystals were dried over phosphorus pentoxide under the reduced pressure of 2—5 mmHg in an atmosphere of nitrogen.

Found: N, 9.22; Cl, 23.38. Calcd. for $C_{12}H_9N_2$-FeCl$_2$: N, 9.20; Cl, 23.13%.

The molar ratio of phenazine to ferrous chloride in the product was estimated from its visible absorption spectra to be 1 : 1.

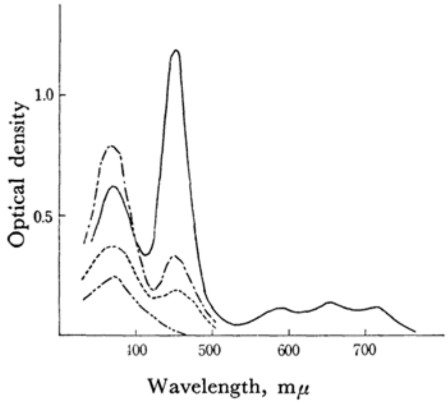

Fig. 1. The visible absorption spectra of a solution of phenazine, stannous chloride and hydrochloric acid (solvent: ethanol).

——: 1.01×10^{-4} mol./l. phenazine, 0.92×10^{-3} mol./l. SnCl$_2$
–·–: 7.23×10^{-5} mol./l. phenazine, 1.81×10^{-5} mol./l. SnCl$_2$
-··-: 2.02×10^{-5} mol./l. phenazine, 22.7×10^{-5} mol./l. SnCl$_2$
----: 4.04×10^{-5} mol./l. phenazine, 4.52×10^{-5} mol./l. SnCl$_2$

Results and Discussion

The Properites of Metal Chelates.—*The Reduction Product with Stannous Chloride and Hydrochloric Acid* (abbreviated as (ph-phH$_2$)$_2$SnCl$_4$).—The reduction product, infusible black-green needle crystals, was completely decomposed to phenazine and stannic chloride when it was dissolved in ethanol, although it was very stable in the crystalline form. The molar ratio of phenazine to stannic chloride in the product was 4 : 1.

The visible absorption spectra of a solution of phenazine, stannous chloride and hydrochloric acid dissolved in ethanol were measured at various

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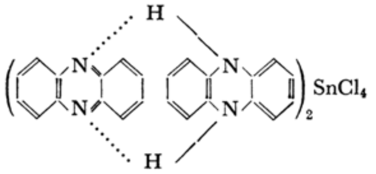
[3] A. Wohl and W. Aue, *Ber.*, **34**, 2442 (1901).

concentrations of the three components, phenazine, stannous chloride and hydrochloric acid. The results are shown in Fig. 1. As can be seen there, a new band appeared at 470 mμ, and the optical density of the new band increased with the increase in the molar ratio of phenazine to stannous chloride. This band seemed to be an absorption of the Sn^{2+}- or Sn^{4+}-chelate. When the concentration of each component in three components was increased, a new band appeared at about 650 mμ. This band must be a charge transfer absorption for phenazhydrin, ph-phH_2. On the other hand, the visible absorption spectrum as measured by the KBr disk showed two bands, at about 378 mμ and 470 mμ, while no band was observed at about 650 mμ.

The infrared absorption spectrum of the reduction product was similar to that of phenazhydrin, ph-phH_2, and showed the absorptions of the $-\overset{|}{N}-H$ band at 3360 cm^{-1}, the $-\underset{|}{\overset{+}{N}}=$ band at 2770 cm^{-1} and the out-of-plane deformation band at 735 cm^{-1}.

From the results described above, the following structural formula may be assigned to the structure of the metal chelate:



The spin concentration, the *g*-value and the half-width of the reduction product as calculated from the ESR spectra are shown in Table I. The ESR spectra consisted of a single narrow band; no fine structures were observed.

The Photo-reduction Product with Isopropyl Alcohol.—The photo-reduction of phenazine with isopropyl alcohol in the presence of ferric chloride gave the Fe^{2+}-chelate as black needle crystals (abbreviated as $phH{\cdot}FeCl_2$). When the crystals were allowed to stand at room temperature in an atmosphere of air for a long time, their color gradually changed from black to yellow. Thus, the photo-reduction product seems to be unstable to oxygen.

The ultraviolet absorption spectrum of an ethanolic solution of the photo-reduction product, $phH{\cdot}FeCl_2$, was found to be identical with that of phenazine because it was oxidized to decompose to phenazine and ferric chloride in the aerated ethanol. Therefore, the photo-reduction was carried out in a closed cell, and the variation in the visible absorption spectra during the course of the photo-reduction was measured. That is, a solution of phenazine and ferric chloride dissolved in isopropyl alcohol was sealed in the closed cell in an atmosphere of nitrogen and irradiated at room temperature for 95 hr. with a 100 W. mercury lamp; then the variation in its visible absorption spectrum with the reduction time was traced. As can be seen in Fig. 2, the absorption of phenazine at about 370 mμ decreased, while a new absorption appeared at about 500 mμ. The new band seems to be that of *N*-monohydrophenazyl, phH·

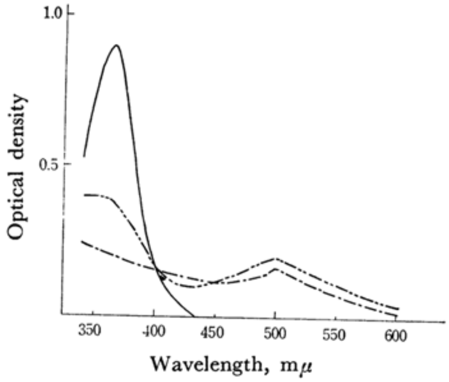


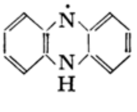
Fig. 2. The visible absorption spectra of the irradiated solution of phenazine in the presence of $FeCl_3$ or $SnCl_4$: Irradiated time; 95 hr. for $FeCl_3$ and 71 hr. for $SnCl_4$, Concentration; $FeCl_3$, 5.3×10^{-5} mol./l., $SnCl_4$, 6.09×10^{-5} mol./l. and phenazine, 6×10^{-5} mol./l.
—— Before irradiation, —·— $FeCl_3$,
—··— $SnCl_4$

Its infrared absorption spectrum was similar to that of $(ph\text{-}phH_2)_2SnCl_4$. However, the out-of-plane deformation band showed the doublet at 740 cm^{-1} and 750 cm^{-1}, such as that of phenazine or dihydrophenazine.

The ESR spectrum was broad, although the features of the spectrum were similar to those of $(ph\text{-}phH_2)_2SnCl_4$. The *g*-value was large in comparison with that of the free electron, as is shown in Table I.

On the other hand, the ultraviolet and infrared spectral properties of the photo-reduction product obtained in the presence of stannic chloride (abbreviated as $phH{\cdot}SnCl_2$) were similar to those of $phH{\cdot}FeCl_2$, but the ESR spectrum was different, as is shown in Table I and Fig. 2.

As has been described above, the Fe^{2+}- and Sn^{2+}-chelates obtained by the photo-reduction both have free spins, and its visible spectrum shows an absorption at about 500 mμ. Also, the infrared spectrum shows an absorption of the $-\underset{|}{\overset{+}{N}}=$ band; the molar ratio of the phenazine ring to ferrous chloride or stannous chloride is 1 : 1. Hence, the structural formula of the metal chelate might be formulated as follows:



$FeCl_2(SnCl_2)$

Namely, the intermediate photo-reduction product of phenazine would form the metal chelate with the Fe^{2+} or Sn^{2+} ion obtained by the photoreduction of the Fe^{3+} or Sn^{4+} ion.

Electrical Conductivities.—The d. c. resistivity was measured under the pressure of 10^3 kg./cm² in vacuo according to the methods described in a previous paper.⁴⁾ In the case of $phH{\cdot}FeCl_2$ or $SnCl_2$, the d. c. measurement was carried out with especial caution because it is unstable to oxygen. The dark-currents of all the metal chelates were ohmic up to 10^3 V./cm. The relationships between the d. c. resistivity and the temperature are shown in Fig. 3. The resistivity at an ascending temperature coincided with that at a descending temperature, and a linear relationship between $\log \rho$ and $1/T$ was observed. The value of $\Delta\varepsilon$ was calculated by the following equation:

$$\rho = \rho_0 \exp(\Delta\varepsilon/2\boldsymbol{k}T)$$

where $\Delta\varepsilon$ is the apparent energy gap; $\boldsymbol{k}$ is the Boltzman constant, and ρ is a specific electrical resistivity. The values of ρ_{20} and $\Delta\varepsilon$ are shown in Table I, which the values of ph-phH_2 are those reported in our previous paper.⁴⁾ The ρ_{20} values of all metal chelates were lower by about 10^2—10^5 than that of ph-phH_2. The ρ_{20} of $(ph\text{-}phH_2)_2SnCl_4$ was the lowest among those of all the metal chelates. The reason for this may be that the molecular arrangement of ph-phH_2 is more regular than that of the other chelates.

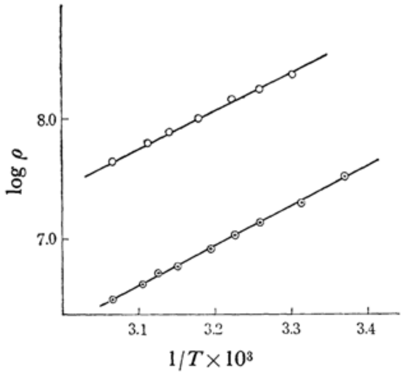


Fig. 3. The relationship between $\log \rho$ and $1/T$.
-○- $phH{\cdot}SnCl_2$ -⊙- $phH{\cdot}FeCl_2$

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4) H. Inoue, S. Hayashi and E. Imoto, This Bulletin, **37**, 336 (1964).