# The Electron Paramagnetic Resonance Spectrum of Silver Phthalocyanine[1]

BY A. MacCragh AND W. S. Koski

The electron paramagnetic resonance spectrum of silver(II) phthalocyanine has been studied in 1-chloronaphthalene at 77°K. and in the solid state at room temperature. The nitrogen hyperfine structure was observed and its spacing shows that the odd electron can be found in the silver $d_{x^2-y^2}$ orbital about 54% of the time. The g-values ($g_\parallel = 2.093$, $g_\perp = 2.017$) and Hamiltonian parameters are compared to those found for copper phthalocyanine and silver porphyrin.

## Introduction

The electron paramagnetic resonance spectra of copper(II) etioporphyrin (II),[2] copper (II) phthalocyanine,[3] and silver(II) deuterioporphyrin IX dimethyl ester[4] have been reported and discussed from this Laboratory. To proceed with the investigation of the variation in bonding parameters for metals in the same column of the periodic table and in similar coordinating environments, an e.p.r. study of silver phthalocyanine was undertaken.

nines, on the one hand, and that of silver phthalocyanine on the other, have been attributed, at least in part, to the monovalent character of the metal in the latter case.[9]

## Experimental

Silver(II) phthalocyanine (Fig. 1) was obtained from the exchange reaction of dilithium phthalocyanine (prepared from phthalonitrile and lithium hydride) in alcoholic silver nitrate. The optical spectrum of the product (in 1-chloronaphthalene), scanned from 900 to 330 mμ, showed absorption bands at 677, 649, 611, and 348 mμ, in comparison with 684, 653, 615, and 348

TABLE I

HAMILTONIAN PARAMETERS OF METALLOPHTHALOCYANINES AND PORPHYRINS

| | | | | Nitrogen hyperfine constants $\times 10^{-3}$ cm.$^{-1}$ | | | | |
|---|---|---|---|---|---|---|---|---|
| | $g_0$ | $g_\parallel$ | $g_\perp$ | $\|b'\|$ | $\|C\|$ | $\|D\|$ | $\alpha'$ | $\alpha^2$ |
| Cu$^{++}$ phthalocyanine in H$_2$SO$_4$ | 2.085 | 2.180 | 2.037 | 1.44 | 1.39 | 1.47 | 0.57 | 0.72 |
| Ag$^{++}$ phthalocyanine in 1-Cl-naphthalene | 2.042 | 2.093 | 2.017 | 2.26 | 2.14 | 2.32 | .71 | .54 |
| Ag$^{++}$ porphyrin in 1-Cl-naphthalene | 2.057 | 2.110 | 2.031 | 2.26 | 2.20 | 2.29 | .71 | .54 |

From the first synthesis of this compound, there had been some doubt as to whether it contained silver in the mono- or in the divalent state,[5] although the
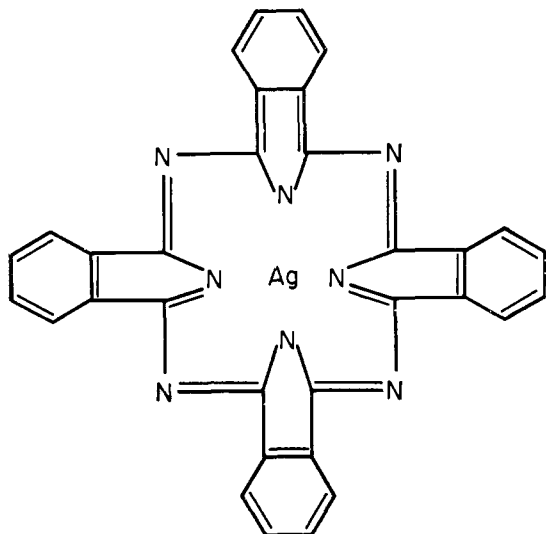


Fig. 1.—Silver phthalocyanine.

corresponding porphyrins were known to be compounds of Ag(II).[6] Recently both formulations have appeared in the literature.[7,8] The marked differences found between the infrared spectra of both labile (Mg) and stable (Zn, Cu, Fe, Co, Ni) covalent phthalocya-

mμ for copper phthalocyanine. A paramagnetic impurity, which gave a sharp e.p.r. line about 6 gauss in width and of $g_0 = 2.003$ ($\pm 0.001$)[8,10] was eliminated by washing the polycrystalline material repeatedly with ethanol and benzene.

Paramagnetic resonance spectra of powdered silver phthalocyanine at room temperature and of its solution in 1-chloronaphthalene at 77°K., were taken with a Varian model V 4500 spectrometer, utilizing 100 kc. modulation. The microwave frequencies were 9.532 and 9.144 kMc./sec., respectively.
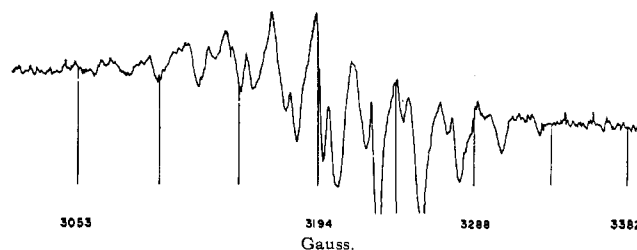


Fig. 2.—The electron paramagnetic resonance (derivative) spectrum of silver phthalocyanine in 1-chloronaphthalene at 77°K.

The main experimental difficulty lay in the very low solubility of silver phthalocyanine (of the order of $10^{-5}$ M even in 1-chloronaphthalene, the best known solvent)[11] and in its ready decomposition in solution to the metal-free compound. Supersaturated solutions (approximately $10^{-3}$ M) were obtained by distilling the solvent at reduced pressure from solutions saturated at 100°. The paramagnetic spectra were taken immediately after preparation of the samples, before appreciable precipitation had begun.

## Discussion

The same procedure was followed for the analysis of the frozen solution spectrum as in the case of the previously investigated compounds.[2,4] The odd electron is placed in the antibonding B$_{1g}$-orbital

$$B_{1g} > \; = \; \alpha|d_{x^2-y^2}> \; \pm \; \frac{\alpha'}{2}\,[|h_1> \; - \; |h_2> \; - \; |h_3> \; + \; |h_4>]$$

where the $|h_i>$ are hybrid orbitals constructed from combinations of the nitrogen 2s- and 2p-orbitals, and

(1) This investigation was supported in part by research grant RG-5144 from the Division of General Medical Sciences, Public Health Service, National Institutes of Health.

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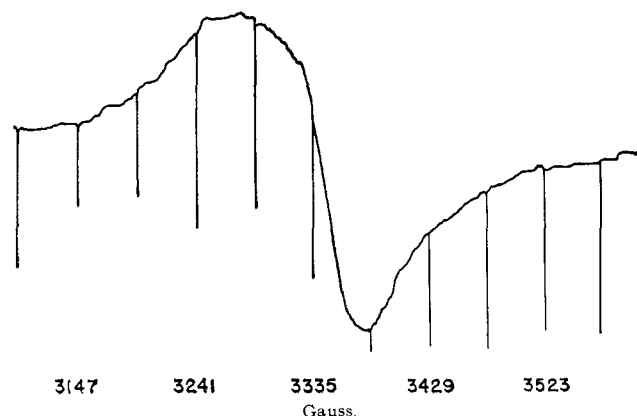(11) J. S. Anderson, et al., J. Chem. Soc., 1151 (1938).

Fig. 3.—The electron paramagnetic resonance (derivative) spectrum of polycrystalline silver phthalocyanine at room temperature.

$d_{x^2-y^2}$ is a silver 4d-atomic orbital. Overlap is included in the $B_{1g}$-orbital and related to the coefficients $\alpha$ and $\alpha'$, by $\alpha' = {}^1/_2\alpha S + \sqrt{1 - \alpha^2}$, where $S$ is taken to be 0.1. The spin Hamiltonian of an electron in a tetragonal electric field can be written as

$$3C_s = g_{\|}\beta_e(H_zS_z) + g_{\perp}\beta_e(H_yS_y + H_xS_x) + A(S_zI_z^{Ag}) + B(S_yI_y^{Ag} + S_xI_x^{Ag}) + C(S_zI_z^N) + D(S_yI_y^N + S_xI_x^N)$$

The parameter $b' = {}^1/_3(2D + C)$, is related to the molecular orbital coefficient $\alpha'$ by

$$(\alpha')^2 = \frac{9b'hc}{4\pi\gamma_N\beta_e\beta_N |\rho_N(0)|^2}$$

where $\gamma_N = 0.4037$ and $|\rho_N(0)|^2 = 33.4 \times 10^{24}\ \mathrm{cm.}^{-3}.^2$

The best values for the resonances corresponding to $H_{\perp}$ and $H_{\|}$ (Fig. 2) are given by:

$$H_{\perp}(\text{gauss}) = 3238.7 - 33.9m_1 - 24.6m_2$$
$$H_{\|}(\text{gauss}) = 3120.0 - 75.1m_1 - 21.9m_2$$

which correspond closely to the spectrum of silver(II) porphyrin.[4] The Ag nuclear spin, $\pm{}^1/_2$, is $m_1$, and $m_2 = \pm 4, 3, \ldots, 0$, the total $N^{14}$ nuclear spin.

The results are compared to those for copper phthalocyanine and silver porphyrin in Table I.

From the paramagnetic resonance spectrum of polycrystalline silver phthalocyanine (Fig. 3), the value of $g_{\perp}$ could be determined by the method of Kneubühl[12] and was found to be 2.016 ($\pm0.001$), in close agreement with that for the frozen solution.

Although the $B_{1g}$-molecular orbital is covalent, for the odd electron can be found in the silver $d_{x^2-y^2}$ orbital about 54% of the time, silver phthalocyanine, in contrast to copper phthalocyanine, is readily demetallized by strong acids. This has been attributed in general to the labile covalent metallophthalocyanines because of the unfavorable relation between the radius of the metal and the space available for it within the isoindole group.[13]

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# The Effect of Ionic Hydration on Rate and Equilibrium in Concentrated Alkaline Solutions. I. The $H_-$ Function in Aqueous Alkaline Solutions and the Hydration of the OH⁻ Ion[1]

BY GAD YAGIL AND MICHAEL ANBAR

The values of the indicator acidity function $H_-$ in concentrated aqueous NaOH and KOH solutions were calculated by applying the theory of Bascombe and Bell to alkaline solutions. It was found that the assumption of a hydration number of three for the OH⁻ ion, as suggested by Ackermann, leads to calculated values which are in good agreement with the experimental results of Schwarzenbach and Sulzberger.

The indicator acidity function[2b] concept has been extensively applied in the interpretation of rate data of acid-catalyzed reactions in concentrated acid solutions.[2a,b] Little work has been carried out concerning base-catalyzed reactions in concentrated alkaline solutions. The $H_-$ function has been measured in methanolic alkaline solutions[3a] and it was shown that the rate of a typical B-1 reaction, namely the hydrolysis of chloroform, follows that function in concentrated methoxide solutions.[3b] The values of $H_-$ in aqueous solutions of NaOH and KOH had been determined by Schwarzenbach and Sulzberger.[4] These values were criticized on account of the method of measurement.[5] However, recently reported rate data show nearly linear correlation with the experimental values of Schwarzenbach for $H_-$; the reactions measured include the hydrolysis of chloramine and dimethylchloramine[6] and the reaction of chloramine with ammonia.[7] It is

the purpose of this and the following publication[8] to evaluate the information which can be obtained on the mechanism of a base-catalyzed reaction from rate measurements in concentrated alkaline solutions. In this first part, a current theory regarding the origin of the acidity function phenomenon will be applied to alkaline solution, leading to a discussion of the state of hydration of the hydroxyl ion in these solutions. This information will be applied in part II[8] to formulate the relations between reaction rate and basicity, and some experimental data supporting the conclusions will be presented.

The indicator acidity functions, treated originally as empirical concepts, have recently been rationalized by Bascombe and Bell,[9,10] who showed that the high acidities encountered in concentrated acid solutions are primarily due to the strong hydration of the proton in these solutions. The existence of protons in a tetrahydrated form $(H_9O_4^+)$ has been suggested by many investigators using a variety of experimental techniques.[11-17] When the hydration of the proton is

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