benzene layer separated and dried with anhydrous calcium sulfate. The benzene was removed by distillation and the deep-red, semisolid residue was sublimed at 45–55° (10 mm.) to give 1.4 g. (83%) of π-allyl-π-cyclopentadienylpalladium, as deep-red needles, m.p. 60–62° (dec.).

Anal. Calcd. for $C_8H_{10}Pd$: C, 45.2; H, 4.7; mol. wt., 212. Found: C, 45.2; H, 5.0, 4.7; mol. wt., 190, 184.

Its ultraviolet and visible spectra were measured in isooctane: λ max. 470 mμ (ϵ, 225); λ max. 315 mμ (ϵ, 6,740); λ max. 257 mμ (ϵ, 25,200); λ max. (shoulder) 225 mμ (ϵ, 8,950).

π-Allyl-π-cyclopentadienylnickel.—A mixture of 10 ml. of freshly prepared cyclopentadiene and 50 ml. of anhydrous pentane was cooled with an ice-bath under an argon atmosphere. The mixture was rapidly stirred as 21 ml. of an 0.24 M (~0.05 mole) solution of n-butyllithium in hexane was slowly added. The solvents were removed *in vacuo* with the exclusion of air and moisture. The resultant cyclopentadienyllithium was dissolved in 100 ml. of anhydrous tetrahydrofuran that had been deoxygenated by purging with nitrogen. The pale yellow solution of cyclopentadienyl-

lithium was stirred under nitrogen and 6.5 g. (0.05 mole) of anhydrous nickel(II) chloride was added. After the characteristic green color of bis-(π-cyclopentadienyl)-nickel appeared, 24 ml. (0.05 mole) of a 2.1 M solution of allylmagnesium chloride in tetrahydrofuran was added. A deep red color rapidly formed. The reaction mixture was stirred for 2 days at 0°. Most of the tetrahydrofuran was removed by distillation at 0° (100 mm.). The red residue was purified by trap-to-trap distillation at ~50° (0.45 mm.), and arbitrary cuts were examined by n.m.r. The yield was about 50%. A middle fraction was analyzed.

Anal. Calcd. for $C_8H_{10}Ni$: C, 58 4; H, 6.1; Ni, 35.5. Found: C, 58.5; H, 6.3; Ni, 32.9.

π-Allyl-π-cyclopentadienylnickel was also prepared by the reaction of equivalent amounts of *bis*-(π-cyclopentadienyl)-nickel and allylmagnesium chloride in tetrahydrofuran.

An Electron Spin Resonance Study of Silver Porphyrin[1]

By Fritz K. Kneubühl, W. S. Koski and W. S. Caughey

The electron spin resonance spectrum of silver(II) deuteroporphyrin IX dimethyl ester has been studied in chloroform solution at ambient temperatures and in castor oil solution at temperatures ranging from -128 to $+178°$. The spectra that were obtained could be best interpreted by assuming that the silver isotropic splitting was about twice the nitrogen splitting with overlap of the nitrogen hyperfine lines leading to eleven equally spaced components. The g- values and the Hamiltonian parameters are evaluated. The significance of the data to the nature of the metal–nitrogen bond is discussed.

Introduction

The bulk magnetic susceptibility has long been used to study chemical binding in metallic complexes, and in recent years electron spin resonance (e.s.r.) techniques have been brought to bear on the problem. In this Laboratory the latter technique is being used to investigate the metal–nitrogen bond in biologically significant complexes such as the porphyrins. Results of the e.s.r. studies of some vanadyl etioporphyrins[2a] and of copper etioporphyrin[2b] II recently have been published. It is of interest to our program to extend these studies to other porphyrins containing chemically related metals so that the variation of the bonding parameters can be examined as one proceeds through a family of metals in a column of the Periodic Table. This publication gives the result of an e.s.r. study of the Ag^{+2} complex of deuteroporphyrin IX dimethyl ester. The general procedure used in this paper is the same as that of Roberts and Koski in their study of the corresponding copper complex.[2b] Measurements have been made on solutions of low and high viscosity and in glasses. In the latter two cases the method recently outlined by O'Reilly,[3] Sands[4] and Kneubühl[5] was used to analyze the data.

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

(2) (a) E. M. Roberts, W. S. Koski and W. S. Caughey, *J. Chem. Phys.*, **33**, 591 (1961). (b) E. M. Roberts and W. S. Koski, *J. Am. Chem. Soc.*, **82**, 3006 (1960).

(3) D. E. O'Reilly, *J. Chem. Phys.*, **29**, 1188 (1958).

(4) R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).

(5) F. K. Kneubühl, *J. Chem. Phys.*, **32**, 1074 (1960).

Experimental

A Varian Associates Model V 4500 electron paramagnetic resonance spectrometer using 100 kc./sec. modulation was used for the measurements reported here. The microwave frequency was kept constant at 9120 Mc./sec. The magnetic field was monitored with a Harvey-Wells Electronic Inc. Model 501 nuclear magnetic resonance gaussmeter.

The sample of silver(II) deuteroporphyrin IX dimethyl ester (Fig. 1) used in this study was prepared from highly purified deuteroporphyrin IX dimethyl ester and silver carbonate in glacial acetic acid solution. Recrystallization from benzene gave a product melting at 204–205°. Elemental analyses for carbon, hydrogen nitrogen and silver yielded values in close agreement with the theoretically expected values. The detailed experimental procedure for the preparation of this compound will be described in detail elsewhere.[6] The chloroform and castor oil solutions used ranged in concentrations from 10^{-2} to 10^{-3} molar.

Theory

It will be assumed that the electric field at the silver atom has D_{4h} symmetry. This assumption appears to be justified since it was shown in the corresponding copper case and in a number of vanadyl porphyrins that substitution on the periphery of the molecule did not noticeably influence the resonance.

The molecular orbitals were constructed only from the atomic orbitals centered on the nitrogen and silver atoms since there were no observable effects of other atoms on the resonance.

If one follows the procedure used in the copper porphyrin case, the odd electron may be placed in the antibonding B_{1g} orbital.
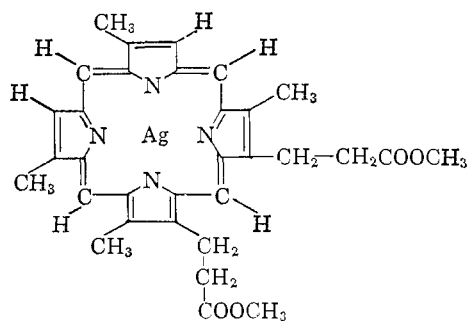
(6) W. S. Caughey, to be published.

Fig. 1.—Silver (II) deuteroporphyrin IX dimethyl ester.

$$|B_{1g}> = \alpha|d_{x2-y2}> - \frac{\alpha'}{2}\,[|h_1> -$$
$$|h_2> - |\,|h_3> + |h_4>]\quad (1)$$

where the $|h_i>$ are hybrid orbitals constructed from appropriate combinations of the nitrogen 2s and 2p atomic orbitals, and d_{x2-y2} is the silver 4d atomic orbital. Overlap is included in the B_{1g} orbital and is related to the coefficients α and α' by

$$\alpha' = {}^1/_2\alpha S + \sqrt{1-\alpha^2}\quad (2)$$

S has been calculated as 0.1 for the copper complex and a similar value is being assumed for the silver case.

If one grants a tetragonal electric field, the spin Hamiltonian of an electron in such a field can be written as

$$H_s = \beta g_{||}H_zS_z + \beta g_\perp\,(H_yS_y + H_xS_x) + AS_zI_z^{Ag} +$$
$$B(S_yI_y^{Ag} + S_xI_x^{Ag}) + CS_zI_z^N + D(S_yI_y^N + S_xI_x^N)\quad (3)$$

where the z axis is the symmetry axis of the molecule and the other symbols have their usual significance.

If one deals with solutions of low viscosity, the anisotropic parts of the Hamiltonian vanish and one obtains

$$H_s = g_0\beta eHS_z + \alpha'\overrightarrow{S\cdot I}^{Ag} + b'\overrightarrow{S\cdot I}^N$$

$$b' = \frac{4\pi\nu_N\beta_e\beta_n}{9}\,(\alpha')^2\,|\rho_N(0)|^2$$

$$g_0 = {}^2/_3g_\perp + {}^1/_3g_{||}\quad \alpha' = {}^2/_3B + {}^1/_3A$$
$$b' = {}^2/_3D + {}^1/_3C\quad (4)$$

The coefficient b' arises from the Fermi contact term and is related to α' which in turn is related to α^2 through the overlap S. α is a measure of the contribution of nitrogen orbitals to the molecular orbital; consequently it is of significance as far as the nature of the orbital containing the odd electron is concerned.

The parameters of the anisotropic spin Hamiltonian are determined from the spectra of glasses and highly viscous solutions. A simplified method similar to the one outlined previously by Sands[4] and others has been used in this work. It consists of superimposing and differentiating hypothetical line shapes of the form

$$S(H_s) = {}^2/_3\,\frac{M}{(H_\perp - H_{||})^2}\,|H_s + H_\perp - 2H_{||}|$$

$$= 0 \text{ if } |2H_s - H_\perp - H_{||}| > |H_\perp - H_{||}|$$

$$g_\perp\,\beta eH_\perp = h\nu - Bm_1 - Dm_2$$
$$g_{||}\,\beta eH_{||} = h\nu - Am_1 - Cm_2$$

where $m_1 = \pm{}^1/_2$ and $m_2 = \pm 4, \pm 3, \ldots\ldots\ldots, 0$
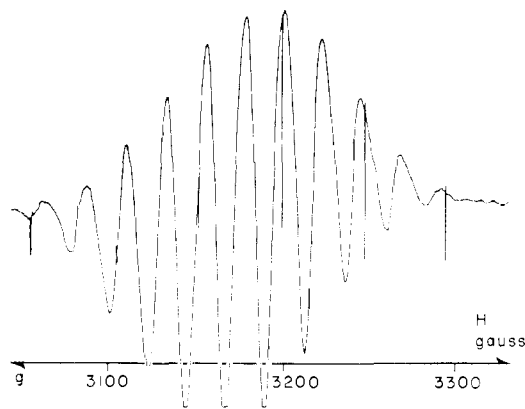$$(5)$$

Fig. 2.—First derivative of the e.s.r. spectrum of silver porphyrin in chloroform at room temperature.

M represents the intensity factor given by a multinomial distribution expected for the four nitrogen spins. The $S(H_z)$ used here is a simplified form of the theoretically derived ideal line shapes of Searl, Smith and Wyard[7] and of others.[5] The application of this simplified form of $S(H_z)$ to the case of the vanadyl porphyrins and others has demonstrated its value for the determination of the anisotropic spin parameters. The use of the much more complicated theoretical curves for this purpose does not seem to be of any particular advantage.

Results and Discussion

The silver nuclei of interest here have spins of ${}^1/_2$ and are surrounded by four equivalent nitrogens each of which has a spin of unity. If the resolution were complete the isotropic (e.s.r.) spectra would be expected to show two sets of nine lines with an intensity of 1:4:10:16:19:16:10.4:1 as given by the multinomial distribution. These lines can be slightly altered by broadening and saturation effects.[8] The centers of the individual lines would be expected to be located at

$$H_s\,(m_1, m_2) = H_0[1 - {}^1/_2(a'/H_0)^2\,I_1\,(I + 1) - {}^1/_2(b'/H_0)^2\,I_2(I_2 + 1)] - a'm_1[1 - {}^1/_2(a'/H_0)m_1]\cdot$$
$$b'm_2[1 - {}^1/_2(b'/H_0)m_2]\quad (6)$$

The isotropic spectrum obtained for the silver porphyrin in chloroform solution is given in Fig. 2. The pattern is a symmetric one consisting of eleven lines of an equal separation of 21.1 gauss and with an approximate peak ratio of 6:16:36:62: 89:100:89:62:36:16:6. This can be best explained by assuming an overlap of the 2 sets of nine nitrogen hyperfine lines. If one assumes the $a'/b' = 2$ and neglects all broadening effects, the resulting peak ratio obtained from a synthesized spectrum is 3:12:34:62:90:100:90:62:34:12:3. By introducing a small Gaussian broadening of the individual lines, one can easily change the ratio to 4:14:35:63: 90:100:90:63:35:14:4. The relatively high experimental values found for the smallest peaks indicate saturation effects and small deviation from Gaussian to Lorentzian line shapes. Trials with other ratio a'/b' failed to give better agreement with experiment. For example, if $a'/b' = 4$ and neglect-

(7) J. W. Searl, R. C. Smith and S. C. Wyard, Proc. Phys. Soc., 74, 491 (1959).

(8) M. J. Stephen and G. K. Fraenkel, J. Chem. Phys., 32, 1435 (1960).

TABLE I

SPIN HAMILTONIAN PARAMETERS OF METALLO PORPHYRINS

Porphyrin	g_0	$g\|$	$g\perp$	$\|a'\|$	$\|A\|$	10^{-3} cm.$^{-1}$ $\|B\|$	$\|b'\|$	$\|C\|$	$\|D\|$	α'
Cu^{++}	2.097	2.169	2.062	8.9	18.8	3.9	1.4	1.3	1.5	0.55
Ag^{++}	2.054	2.104	2.029	4.4	7.1	3.1	2.2	2.0	2.3	0.69
Ag^{++}	2.054	2.093	2.039	4.4	3.9	4.7	2.2	2.0	2.3	0.69
			2.034							

ing broadening effects, one gets peak ratios of 5:20:50:80:100:100:100:100:100:80:50:20:5. Thirteen peaks are to be expected but actually only eleven are observed. Even if one assumes that the two small ones are not observable, it is clear that the intensity distribution is very different from the observed situation.
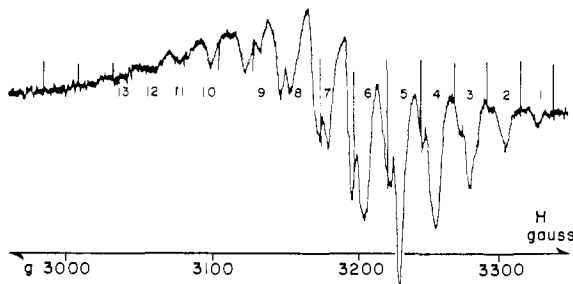

Fig. 3.—First derivative of the e.s.r. spectrum of silver porphyrin in castor oil at −128°. Numbers are included for comparison of spectra in Figs. 3 and 5.

Solutions of the porphyrin in a viscous solvent (castor oil) were investigated from −128 to 178°. Figure 3 shows a typical spectrum that was obtained at −128°, and it is from this curve that the anisotropic Hamiltonian parameters were determined. As the temperature was raised from −128°, there was no pronounced change in the spectra up to 22°, although at the latter temperature broadening did obscure some of the structure visible at −128° as is evidenced in Fig. 4. On further increase in temperature, the spectra gradually changed until they then took on the typical form exhibited by the isotropic spectrum shown in Fig. 2. It is possible to reconstruct the anisotropic resonance by assuming that the line shapes are given by equation 5. The best values for the resonances corresponding to $H_\perp$ and $H_{||}$ are given by

$$H_\perp(\text{gauss}) = 3212.4 - 34.4m_1 - 24.6m_2$$
$$H_{||}(\text{gauss}) = 3095.0 - 72.0m_1 - 20.0m_2 \qquad (7)$$

By using eq. 5, introducing some line broadening and differentiating, one obtains a curve (Fig. 5) which is practically identical with the experimentally observed one shown in Fig. 3. The various Hamiltonian parameters obtained for the silver porphyrin are summarized in Table I where the corresponding data for the copper porphyrin are included for comparison.

The shape of the spectrum can also be explained by assuming a small splitting of $g_\perp$ into g_2 and g_3. The Hamiltonian parameters for this situation are included in the row indicated by the asterisk in Table I. In view of the fact that none of the metallic porphyrins studied have shown noticeable deviations from tetragonal symmetry and since a comparison of the parameters $|A|$ and $|B|$

with corresponding parameters of the copper porphyrin indicates that the initial assumption of only two g factors gives a consistent interpretation, the assumption of the splitting of $g\perp$ is not necessary. It is mentioned here, however, since it is another possible interpretation of the data.
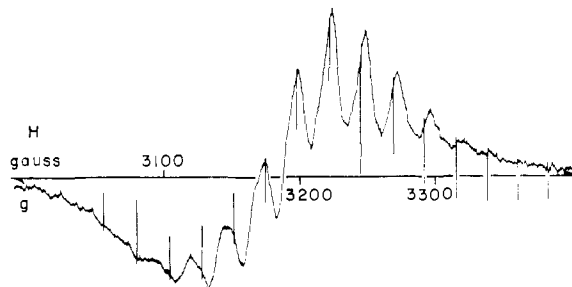

Fig. 4.—Derivative presentation of the e.s.r. spectrum of silver porphyrin in castor oil at 22°.
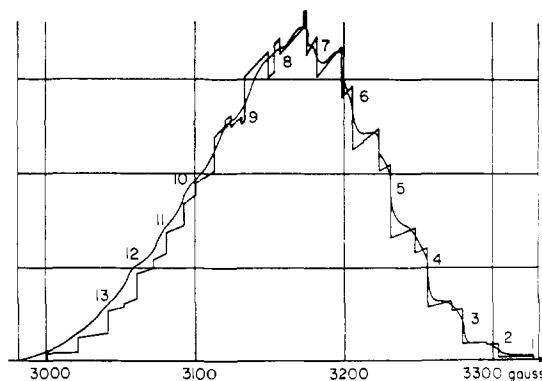

Fig. 5.—Reconstructed spectrum based on equation 6.

The most striking difference in the spectra of these two metal porphyrins is in the nitrogen hyperfine structure. The spacing of 21.1 gauss in the silver porphyrin is considerably greater than the corresponding spacing in the copper compound. The metal hyperfine splittings are also compatible with this observation. These facts are reflected in a quantitative manner in the Hamiltonian parameters listed in Table I. Specifically, if one calculates α^2, assuming an overlap of 0.1 for both copper and silver compounds, values of 0.74 and 0.58, respectively, are obtained. This indicates a considerably greater amount of covalent character in the B_{1g} oribital of the silver compound.

It is interesting to note that no effects of the bridge hydrogens were detected in the resonance. One might expect theoretically that such interactions should be present and their absence could be attributed to both experimental and theoretical factors. This point is being investigated further.