to support Vesely's statement[44] that "the reaction of chain growth proceeds with the participation of free ions and not ionic pairs, as is postulated by many authors." At least, it is probably fair to say that the conclusions arising out of kinetic investigations on conventional ionic polymerization are equivocal on this question.[45] However, there are at least two cases where the results appear to suggest that the propagation reaction is extremely fast when a *free* (or partially free) ion is involved. First, the work of Kennedy and Thomas[46] on the cationic polymerization of isobutene at $-78°$ led them to suggest that under certain conditions, the growth of the chain could take place by a diffusion-controlled mechanism with a time for single monomer addition $(1/k_p[M])$ of about 8×10^{-11} sec. Since [M] was about $1.5\ M$ in these experiments, this would indicate a value of $k_p \sim 8 \times 10^9\ M^{-1}$ sec.$^{-1}$. It should be added that the authors[46] expressed the view that the reaction is probably not quite as rapid as their calculation would indicate. The second example comes from the recent work of Szwarc and his co-workers[47] on the anionic polymerization of styrene in tetrahydrofuran. These authors have shown that the propagation

rate constant for the free anion is $6.5 \times 10^4\ M^{-1}$ sec.$^{-1}$, whereas the corresponding value for the ion pair lies in the range between 120 and 200 M^{-1} sec.$^{-1}$, depending on the alkali metal counterion. Thus, since it is quite probable that many previous kinetic results reflect composite behavior due to free ions and ion pairs, the high reactivity of the free ion has not been fully realized because the concentration of free ions is generally very small by comparison with ion pairs under the usual polymerization conditions. It is clear that more work is required to resolve the position.

In conclusion, the high value for k_p obtained in this investigation appears to support Dainton's general contention[48] that propagation by unhindered cations is considerably faster than by free radicals. Although our results on the temperature dependence are not entirely unambiguous, the constant rate between -78 and $-30°$ would seem to imply that the activation energy for propagation cannot exceed that for a possible diffusion-controlled termination step, *viz.*, *ca.* 2 kcal./mole.

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(44) K. Vesely, *J. Polymer Sci.*, 52, 277 (1961); the contributions of Vesely and his group have been reviewed by P. H. Plesch in "The Chemistry of Cationic Polymerization," P. H. Plesch, Ed., The Macmillan Co., New York, N. Y., 1963, p. 167 ff.
(45) M. Szwarc, *Advan. Chem. Phys.*, 2, 147 (1959).
(46) J. P. Kennedy and R. M. Thomas, *J. Polymer Sci.*, 49, 189 (1961).
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Electron Spin Resonance of
α- and β-Cobalt Phthalocyanine[1a]

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The magnetic properties of α- and β-cobalt phthalocyanine polymorphs diluted in metal-free, zinc, and nickel phthalocyanine were investigated by e.s.r. The spectra of the two complexes reveal the difference in their polymorphic structures. The Hamiltonian parameters, g-factors and hyperfine splitting constants, determined from polycrystalline samples are compared with single crystal work. The magnetic moment $\mu_{eff} = 2.38$ B.M. obtained for α-cobalt phthalocyanine at room temperature is 15% lower than that in β-cobalt phthalocyanine. The ordering and separation between the energy levels of Co^{+2} are discussed on the basis of the experimental data.

I. Introduction

Phthalocyanine compounds are known to exist in at least three polymorphic forms. The β-form is the most stable polymorph, and its molecular orientation and

crystal structure were extensively studied by Robertson[2a] and others.[2b] The other two polymorphs are the α- and γ-forms. Detailed X-ray analyses of the latter two forms have not been performed, because it has not been possible to grow single crystals of these polymorphs. Differentiation between the three polymorphic complexes is best achieved by comparing their characteristic infrared spectra.[3] Most of the accumulated data in the present literature describing the electrical and magnetic properties of the phthalocyanine compounds correspond to the β-form since most of the samples discussed were prepared by sublimation. The β-phthalocyanine (abbreviated β-Pc) is invariably the only polymorph prepared by sublimation methods, which are found to be the most effective purification and crystal growth processes for these metallo-organic complexes.

(1) (a) Taken in part from a dissertation to be presented by J. M. Assour in partial fulfillment of the requirement for a Ph.D degree; (b) RCA Laboratories, Princeton, N. J.

(2) (a) J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, New York N. Y., 1953; (b) F. H. Moser and A. L. Thomas "Phthalocyanine Compounds," Reinhold Publishing Corp., New York, N. Y., 1963.
(3) D. N. Kendall, *Anal. Chem.*, 25, 382 (1953).

● NITROGEN ATOMS
○ Co ATOM
$r_1 \approx 3.38$ Å
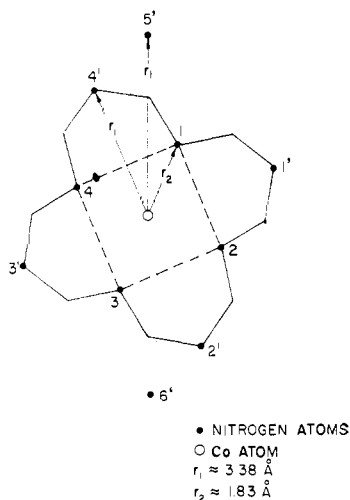$r_2 \approx 1.83$ Å

Figure 1. Position of nearest and next nearest nitrogens with respect to the metallic center.

There is a sharp difference, however, in the electrical properties between the α- and β-forms as was recently reported by Wihksne and Newkirk.[4] These workers found the conductivity of the α-polymorph to be 10^5 times greater than that of the β-polymorph at the transition temperature. They also found that the dark conductivity activation energy of α-phthalocyanine (α-Pc) was reduced by a factor of $\sim$4 in comparison with β-Pc. We have investigated the magnetic properties of the α- and β-forms by e.s.r. To our knowledge this is the first e.s.r. study wherein the spectra of these two complexes clearly reveal their polymorphic character.

Since several phthalocyanine metallic derivatives are known to be paramagnetic (Cu, Co, Mn, Ag, etc.), we have chosen the cobalt derivative (CoPc) for this investigation because of the particular electronic configuration of the Co^{+2} ion. Gibson, Ingram, and Schonland[5] have measured the e.s.r. absorption of CoPc magnetically diluted in ZnPc single crystals. Based on their experimental data, Griffith[6] formulated a theory which accounts semiquantitatively for the observed spectra. Both experimental results and theory strongly suggest that the unpaired electron associated with the Co^{+2} ion is located in a d_{z^2} orbital level which was postulated to be the ground state. Further support for assigning the unpaired electron to the d_{z^2} orbital is found in our CoPc resonance measurements in solutions.[7] The assumption that the d_{z^2} level is raised above the d_{xy}, d_{yz}, and d_{xz} orbital levels[8] is due to the fact that an odd electron located in a d_{z^2} orbital is favorably exposed for perpendicular conjugation. Therefore, in the phthalocyanine crystal environment, additional interaction with extra molecular nitrogen atoms in the octahedral positions (see section II) may raise the d_{z^2} orbital level. Furthermore, allowed hybridization between the 4s and d_{z^2} orbitals will increase the overlap between parallel molecules in the crystal (*i.e.*, along the b-axis) and hence contribute to the raising of the d_{z^2} level.

(4) K. Wihksne and A. E. Newkirk, *J. Chem. Phys.*, **34**, 2184 (1961).
(5) J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discussions Faraday Soc.*, **26**, 72 (1958).
(6) J. S. Griffith, *ibid.*, **26**, 81 (1958).
(7) J. M. Assour, W. K. Kahn, and S. E. Harrison, to be published.
(8) The d-orbitals of the Co^{+2} ion are assumed to be split under the action of a tetragonal crystal field having a D_{4h} symmetry.

In summary, since the e.s.r. spectra of CoPc would seem partially dependent on the physical stacking of the molecules in the crystal, and since the difference between the α- and β-complexes is primarily in their polymorphism, the e.s.r. of CoPc is expected to elucidate these crystallographic changes more so than any other paramagnetic phthalocyanine derivative.

II. Crystallography

The crystal structure of the β-Pc polymorph is monoclinic, belonging to the space group $P2_{1/a}$ with two centrosymmetrical molecules per unit cell. The unit-cell dimensions of the H_2Pc (metal-free), CoPc, ZnPc, and NiPc are given in Table I. The square-planar

Table I. Cell Dimensions of the Monoclinic Phthalocyanine Crystals

Compounds	a, Å.	b, Å.	c, Å.	β
$C_{32}H_{18}N_8$	19.85	4.72	14.8	122° 12'
$C_{32}H_{16}N_8Co$	20.2	4.77	15.0	121° 3'
$C_{32}H_{16}N_8Zn$	19.22	4.87	14.52	120° 2'
$C_{32}H_{16}N_8Ni$	19.9	4.71	14.9	121° 54'

structure of the CoPc molecule was confirmed by X-ray analysis.[2a,9] The physical arrangement of the molecules and their constituent atoms in the monoclinic crystal has already been discussed in detail elsewhere.[10a]

The crystal structure of the α-polymorph was determined for the CuPc derivative by Robinson and Klein.[10b] The crystal is tetragonal and probably belongs to the space group C_{4h}^1-P4/m. The unit-cell dimensions determined by X-ray powder spectra analyses are: $a = 17.36$, $b = 17.36$, $c = 12.79$ Å., and the number of molecules per unit cell is 6. No other X-ray analyses of the α-polymorph have been reported in the literature.

III. Theory

The unpaired 3d electron associated with the cobalt atom would be expected to interact with the ligating nitrogens situated at $\sim$1.83 Å. There are four more nitrogens within the molecule at a distance of 3.38 Å. In the β-polymorph single crystal, each one of the nearest neighbor molecules along the b-axis contributes a nitrogen at this same distance of 3.38 Å. The central cobalt atom may be described as laying at the center of a square-bonded configuration located within a larger octahedral array of nitrogen atoms. In Figure 1 we have sketched the nitrogen environment of the cobalt atom. From the approximate threefold increase of the length of the b-axis and the number of molecules per unit cell in the α-phase, one may infer that the extra molecular nitrogens in nearest molecules do not form the perfect nitrogen octahedron found in the β-phase.

With reference to Figure 1, the cobalt atom is in the center of a square $\sim$2.6 Å. on a side. In reality the four ligating atoms form a parallelogram, the sides of which differ by $\sim$0.04 Å. This asymmetry was observed in

(9) M. A. Porai-Koshits, *Tr. Inst. Kristallogr. Akad. Nauk USSR*, **10**, 117 (1954).
(10) (a) S. E. Harrison and J. M. Assour "Paramagnetic Resonance II," W. Low, Ed., Academic Press, Inc., New York, N. Y., 1963, p. 855; (b) M. T. Robinson and G. E. Klein, *J. Am. Chem. Soc.*, **74**, 6294 (1952).

the spectra of β-CoPc magnetically diluted in β-ZnPc; however, complete symmetry (i.e., fourfold symmetry) was found in the following samples: (1) CoPc diluted in H_2Pc (β-phase); (2) CoPc diluted in NiPc (β-phase); (3) CoPc diluted in ZnPc (α-phase). Assuming tetragonal symmetry, the results are interpreted by the following spin-Hamiltonian

$$\mathcal{H} = \beta[g_{||}H_zS_z + g_\perp(H_xS_x + H_yS_y)] + AS_zI_z + B(S_xI_x + S_yI_y) \quad (1)$$

where β is the Bohr magneton, A and B are the cobalt nuclear hyperfine interaction constants. In the crystal and powder spectra, no evidence of superhyperfine interaction between the unpaired electron and the surrounding ligands was found. In solution spectra,[7] however, we have observed superhyperfine structure due to nitrogens in the axial positions which belong to the solvent molecules. In the present discussion, the nitrogen nuclear interaction is not included in the Hamiltonian.

Since single crystals of α-Pc are not available with present growth techniques, it was necessary to use polycrystalline powder in our e.s.r. experiments. It will be shown below that powder spectra are as informative and as accurate as single crystal work in the case of CoPc. We will follow Sands[11] theory which has been applied[10a, 12, 13] successfully in the interpretation of e.s.r. data for several viscous liquids and polycrystalline samples.

Considering first-order interaction, the condition for e.s.r. is satisfied by the relation[14]

$$h\nu = g\beta H + KM_I \quad (2)$$

where

$$g^2K^2 = (A^2g_{||}^2 \cos^2 \theta + B^2g_\perp^2 \sin^2 \theta) \quad (3)$$

$$g^2 = g_{||}^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta \quad (4)$$

and M_I is the nuclear-spin quantum number. Among nonoriented, noninteracting paramagnetic centers, including nuclear interaction and neglecting quadrupole interaction, Sands[11] has shown that, if axial symmetry exists about the z-axis, the number of absorbing paramagnetic centers is given by

$$\frac{dN}{dH} = \frac{N_0}{2}\left\{\frac{\cos\theta}{g^2}\left[\frac{(g_{||}^2 - g_\perp^2)}{g}H_0 + \frac{2M_I}{\beta}\left(\frac{(Ag_{||}/2)^2 - (Bg_\perp/2)^2}{Kg} - \frac{2K}{g}(g_{||}^2 - g_\perp^2)\right)\right]\right\}^{-1} \quad (5)$$

N_0 is the total number of molecules, $H_0 = h\nu_0/\beta$, and θ is the angle between the applied field, H, and the axis of symmetry of the magnetic complex. The resonance field as a function of the angle θ is given by

$$H = \frac{H_0}{g} - \frac{2M_I}{\beta}(g_{||}^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta)^{-1}[(Ag_{||}/2)^2 \cos^2 \theta + (Bg_\perp/2)^2 \sin^2 \theta]^{1/2} \quad (6)$$

Equation 6 is reduced for two special orientations. The

first, when $\theta = 0$ (H parallel to the axial axis of the molecule), then

$$H_{||} = (H_0/g_{||}) - (M_IA/\beta g_{||}) \quad (7)$$

and the second, when $\theta = 90°$

$$H_\perp = (H_0/g_\perp) - (M_IB/\beta g_\perp) \quad (8)$$

Since for the divalent cobalt atom $S = {}^1/_2$, $I = {}^7/_2$, and the nuclear-spin quantum number $M_I = \pm {}^1/_2, \pm {}^3/_2, \pm {}^5/_2,$ and $\pm {}^7/_2$, eq. 7 and 8 predict the appearance of two sets of eight lines. One set is composed of eight weak lines of varying intensities, equally spaced, and centered around $H_{||}$. The second set consists of eight intense lines also equally spaced and centered around $H_\perp$. The $H_{||}$ and $H_\perp$ groups of lines yield $g_{||}$ and $g_\perp$, respectively. The formulation discussed thus far will be shown to apply to the α-polymorph. In the case of the β-polymorph, second-order interactions must be included.

The second-order interactions account for the unequal spacing of the resonance lines observed in the spectra of the β-polymorph. Bleaney[14] has considered second-order interactions in paramagnetic salts, and these will be examined for the two angles $\theta = 0$ and $\theta = 90°$ required for analysis of the data from polycrystalline samples. For $\theta = 0$, the resonance condition is

$$H_{||} = (H_0/g_{||}) - (AM_I/g_{||}) - B^2[I(I + 1) - M_I^2](2g_{||}H_0)^{-1} \quad (9)$$

and for $\theta = 90°$

$$H_\perp = (H_0/g_\perp) - (BM_I/g_\perp) - (A^2 + B^2)[I(I+ 1) - M_I^2](4g_\perp H_0)^{-1} \quad (10)$$

In the first approximation, the nuclear interaction splits each electronic transition into $2I + 1$ equally spaced levels with separation A or B. Second-order terms in M_I^2 cause a linear change in the separation between the hyperfine lines within a given electronic transition. For $\theta = 0$ and $\theta = 90°$, the separation always increases toward higher fields.

IV. Experimental Results

The microwave resonance equipment was a V-4500 Varian spectrometer. The magnetic field modulation was 100 kc./sec. while the microwave frequency was 9500 Mc./sec. The magnetic field was determined by a Harvey-Wells n.m.r. gaussmeter in conjunction with a Hewlett-Packard 524 D counter. For low temperature experiments, a Varian quartz dewar was used. In all measurements reported here, the derivative of the absorption was recorded.

The phthalocyanine compounds were synthesized by the method of Barrett, et al.[15] α-Pc is generally prepared by dissolving β-Pc in concentrated sulfuric acid and precipitating the α-Pc by pouring the solution slowly into a volume of crushed ice. The precipitate is then filtered and dried in air. Upon heating the α-Pc powder to 300°, the solid is completely reconverted to the β-form. The α- and β-structures were confirmed by X-ray analysis and infrared spectroscopy.[16] Several attempts to prepare the γ-polymorph according to the

(11) R. H. Sands, Phys. Rev., 99, 1222 (1955).
(12) R. Neiman and D. Kivelson, J. Chem. Phys., 35, 156 (1961).
(13) E. M. Roberts and W. S. Koski, J. Am. Chem. Soc., 83, 1865 (1961).
(14) G. Bleaney, Phil. Mag., 42, 441 (1951).

(15) P. A. Barrett, C. E. Dent, and R. P. Linstead, J. Chem. Soc., 1719 (1936).
(16) A. N. Sidorov and I. P. Kotlyar, Opt. Spectry. (USSR), 11, 92 (1961).

Table II. Summary of Experimental Data

Diamagnetic host	Magnetic dilution	Temp., °K.	g	H.F.S.,[a] cm.$^{-1}$
α-ZnPc	1:1000	300, 77, 27	$g_{\parallel} = 2.007 \pm 0.003$	$A = 0.0116 \pm 0.0003$
	1:10000		$g_{\perp} = 2.422 \pm 0.003$	$B = 0.0066 \pm 0.0003$
β-ZnPc	1:1000	77, 27	$g_z = 1.91 \pm 0.01$	$A_z = 0.016 \pm 0.001$
	1:10000		$g_x = 2.92 \pm 0.02$	$A_x = 0.027 \pm 0.001$
			$g_y = 2.89 \pm 0.02$	$A_y = 0.026 \pm 0.001$
β-H$_2$Pc	1:1000	77, 27	$g_{\parallel} = 1.89 \pm 0.01$	$A = 0.016 \pm 0.001$
	1:10000		$g_{\perp} = 2.94 \pm 0.01$	$B = 0.028 \pm 0.001$
β-NiPc	1:1000	77, 27	$g_{\parallel} = 1.89 \pm 0.01$	$A = 0.015 \pm 0.001$
			$g_{\perp} = 2.94 \pm 0.01$	$B = 0.028 \pm 0.001$

[a] H.F.S. = hyperfine splitting

method of Eastes[17] were unsuccessful; in each attempt only the α-polymorph was obtained. CoPc was magnetically diluted in isomorphous crystals such as H$_2$Pc, NiPc, and ZnPc. The ratio of magnetic dilution of cobalt was increased from 1:1000 to 1:10,000. Spectra recorded for both magnetic dilutions did not show any appreciable variation in the line width or separation of the hyperfine lines.

A. α-CoPc. E.s.r. absorption of α-CoPc magnetically diluted in ZnPc was measured at 300, 77, and 27°K. The Hamiltonian parameters, *g*-factors and nuclear hyperfine constants, did not vary with temperature. However, the intensity of the absorption lines increased slightly at low temperatures. In Figure 2, the spectrum recorded at 77°K. exhibits a sharp resonance
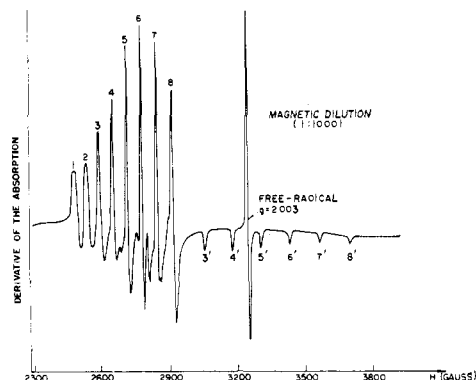

Figure 2. E.s.r. of α-cobalt phthalocyanine magnetically diluted in α-zinc phthalocyanine powder at 77°K.

line flanked on each side by a group of cobalt hyperfine lines. The intense resonance line with $g = 2.003 \pm 0.0005$ is a free-radical resonance characteristic of most phthalocyanine compounds and was investigated previously by Assour and Harrison.[18] The low-field group of lines is composed of eight equally spaced peaks varying in intensity. The separation between the hyperfine lines is 60 ± 3 gauss. The high-field set consists of six visible weak peaks, also equally spaced with a separation 126 ± 3 gauss. Agreement between the observed spectrum and that expected from Sands' theory is clearly shown in Figure 3. The latter figure presents the theoretical distribution of the line centers as calculated from eq. 5 and 6. Note that the resonance lines corresponding to the nuclear transi-

(17) J. W. Eastes, U. S. Patent 2,770,620 (1956).
(18) J. M. Assour and S. E. Harrison, *J. Phys. Chem.*, **68**, 872 (1964).

tions $M_I = \frac{7}{2}$ and $\frac{5}{2}$ belonging to the high-field multiplet are overlapped by the strong transitions $M_I = -\frac{7}{2}$ and $-\frac{5}{2}$ of the low-field multiplet in agreement with Figure 2. The total spectrum exhibits an axial symmetry, and the experimentally determined Hamiltonian constants are given in Table II.
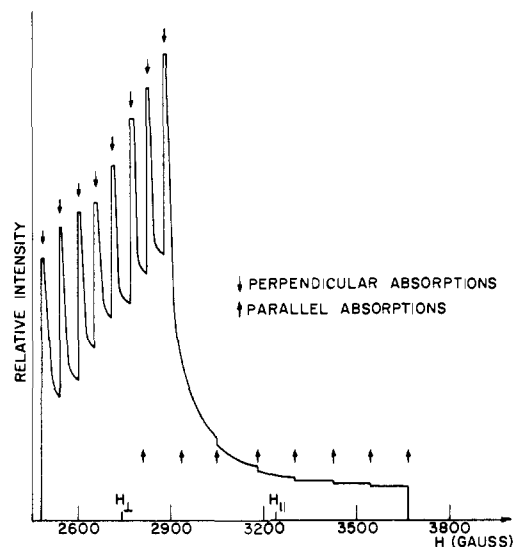

Figure 3. Plot of theoretical distribution of line centers (dN/dH vs. H, eq. 5 and 6).

B. β-CoPc. Upon heating the α-CoPc to 300°, the β-CoPc polymorph is obtained. The e.s.r. spectrum of the α-form was examined after heat treatment at the transition temperature of about 200°. The spectrum revealed a complex structure which appeared to contain admixtures of the α- and β-polymorphs. The new resonance peaks centered around $H_{\perp}$ occurred at lower fields compared with those in Figure 2.

After heat treatment at 300° which lasted for 10 hr., only the e.s.r. spectrum of the β-polymorph was observed. The spectrum seen in Figure 4 was recorded at 77°K. No resonance absorption was observed at 300°K. as reported by Gibson, *et al.*,[5] in their experiments with single crystals. Figure 4 again displays the free-radical resonance and two groups of cobalt hyperfine lines. The low-field structure consists of eight split peaks. The intensity and separation between the peaks increase with the magnetic field. The splitting of each peak is due to the anisotropy of $g_{\perp}$ in the plane of the molecule. This anisotropy was also observed by Gibson, *et al.*,[5] in their experiments on single crystals.
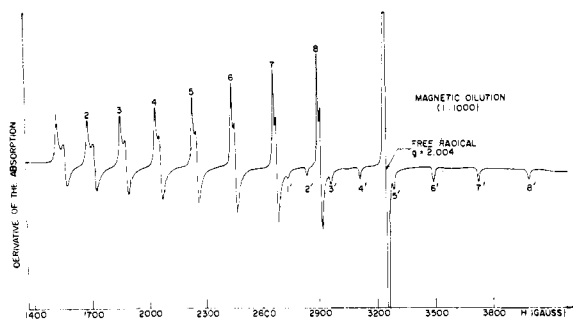
Figure 4. E.s.r. of β-cobalt phthalocyanine magnetically diluted in β-zinc phthalocyanine powder at 77°K.

Figure 5. E.s.r. of β-cobalt phthalocyanine magnetically diluted in β-metal-free phthalocyanine powder at 77°K.

Figure 6. E.s.r. of β-cobalt phthalocyanine magnetically diluted in β-nickel phthalocyanine powder at 77°K.

The high-field set is composed of eight visible but weaker peaks. The spacing between the hyperfine lines is also seen to increase with H. The Hamiltonian parameters for the β-polymorph as determined by the method of Bleaney[14] are given in Table II.

Samples of β-CoPc were also prepared by diluting CoPc in H_2Pc and NiPc. Figures 5 and 6 show the spectrum of each sample recorded at 77°K. Twice more, no resonance absorption was observed at 300°K. All β-polymorph samples are consistent in this respect, and our own single crystal work[7] is in agreement with the absence of the resonance at 293°K. The distribution and spacing between successive hyperfine lines are similar to those in Figure 4. In both spectra of Figures 5 and 6, there is no evidence of splitting in the low-field structure in accord with our single crystal spectra.[7]

A comment concerning the intensity of the free-radial resonance is in order. In our experiments, the free-radical resonance is present in both polymorphs. To show that the origin of the free radical in the cobalt derivative is also due to oxygen absorbed by the phthalocyanine, the following experiment was performed: β-CoPc diluted in H_2Pc powder was packed into a quartz tube which was then evacuated and heat-treated at 300°. The lack of oxygen in the evacuated sample indeed manifested itself in a decrease of the free-radical concentration (Figure 5) in agreement with our previous observations.[18] On the other hand, it should be remarked that the free-radical line width in the NiPc host is about three times broader than those observed in other phthalocyanines. This increase in the NiPc line width was also observed by Ingram and Bennett.[19] Additional experiments are underway to determine the origin of the line broadening in NiPc.

V. Discussion

One of the striking features of the experimental data is the sensitivity of the spin-Hamiltonian parameters of the square-bonded cobalt phthalocyanine to the change in crystal structure, even though the alteration in molecular environment is believed to be small. Since in the β-phase the nearest neighbor molecules have nitrogen atoms at the distance of closest approach, 3.38 Å., the experimental evidence suggests that in the α-phase the nearest neighbor molecules are sufficiently shifted to diminish the interaction between the Co^{+2} ion and the perpendicularly coordinating nitrogens. Thus, we can note that even though the nitrogens in the β-phase do not give rise to a superhyperfine structure, they still

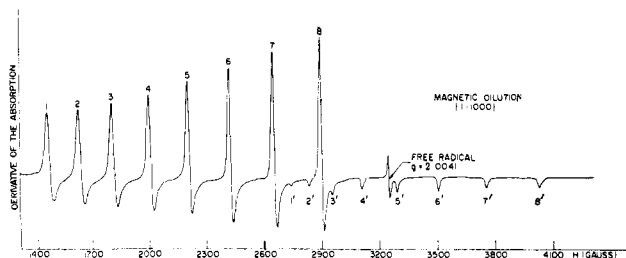(19) D. J. E. Ingram and J. E. Bennett, *Phil. Mag.*, **45**, 545 (1954).
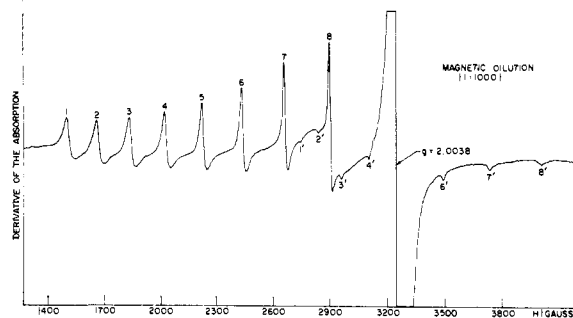
exert a considerable influence on the magnetic properties of the ion.

A second feature is that the symmetry of the guest CoPc molecule in β-host lattices is lowered even though there is no apparent change in the molecular environment in going, e.g., from H_2Pc to ZnPc. It is also of interest to note that in the case of CoPc in the ZnPc host, data obtained from powder spectra appear to be as accurate and complete as that of single crystals.[5] Such an agreement is also found in CoPc diluted in NiPc[7] and CuPc diluted in H_2Pc.[10a] This last result is of importance in e.s.r. experiments, because phthalocyanines are similar in structure with the naturally occurring biological systems such as porphyrins and chlorophyll, and single crystals of many of these complexes are almost impossible to grow.

In the case of the β-polymorph, the low value of $g_{||}$ ($\sim$1.9) has been explained in terms of second-order contributions[6] arising from: (1) admixtures between the 4s and d_{z^2} orbitals, and (2) interactions with the two nitrogen atoms in the octahedral positions along the molecular axis. For α-CoPc the second-order terms vanish, and $g_{||}$ is very nearly equal to the free-electron g-value. If we assume that the ground state of Co^{2+} is d_{z^2}, the spectroscopic splitting factors calculated from second-order perturbation theory are $g_{||} = 2.0023$ and $g_{\perp} = 2.0023 - 6\lambda/\Delta$, where $\Delta = E_{xz,yz} - E_0$ and λ is the spin-orbit coupling constant for the Co^{+2} ion. The latter equations were derived on the basis of a pure crystalline field model; i.e., the cobalt atomic wave functions were chosen from the 3d wave functions. By comparing the value of $\Delta g_{\perp} = (g_{\perp} - 2.0023)$ for the two polymorphs, we find that the separation Δ between the ground state and the E_g state has increased two-fold in going from β-CoPc to α-CoPc. (This larger separation is also found in CoPc solutions.[7]) Thus, in the α-phase where there is a smaller admixture of excited wave functions in
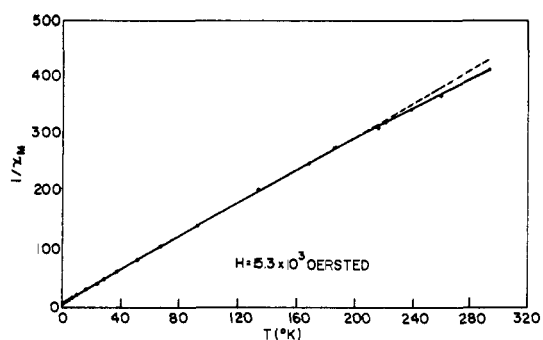
Figure 7. Plot of the reciprocal corrected molar susceptibility *vs.* temperature for powdered α-cobalt phthalocyanine.

the ground state, we would expect to find a larger spin-lattice relaxation. This is borne out by the fact that in our experiments e.s.r. signals of the β-phase samples were not detectable at room temperature while those of the α-phase were observable. The resonances of the α-phase sample were weaker at room temperature than at liquid air temperatures but nevertheless easily detectable. This lack of a signal of the β-phase at room temperature seems to be in disagreement with previous findings.[5]

Additional proof for the greater contribution of orbital moment to the β-phase ground state is also demonstrated by the magnetic susceptibility data. Figgis and Nyholm[20] measured the magnetic susceptibility of several cobaltous compounds, including CoPc. These co-workers failed to mention which CoPc polymorph was investigated; however, their data strongly suggest that it was the β-CoPc. The magnetic moment measured by Figgis and Nyholm at 90°K. is μ_{eff} = 2.22 B.M., and that at room temperature is μ_{eff} = 2.72 B.M. The magnetic moment of β-CoPc was also measured at room temperature by Havemann, *et al.*,[21] and was found to be μ_{eff} = 2.73 B.M. A plot of the reciprocal molar susceptibility *vs.* temperature for the α-CoPc is shown in Figure 7. To the molar susceptibility we added a correction for the diamagnetic susceptibility of the phthalocyanine molecule including that the of paramagnetic cobalt atom.[21] A straight line is indicated from 1.4 to about 230°K. with a negligibly small value for the Curie constant, *i.e.*, $\theta \sim 2$°K. The effective magnetic moment calculated from Figure 7 at 1.4 to 230° K. is μ_{eff} = 2.2 B.M. and that at 293°K. is μ_{eff} = 2.38 B.M. Magnetic moments measured in both phases are larger than the spin-only value of 1.73 B.M. This rather large value of the magnetic moment leads to the suppo-

sition that incomplete quenching of the orbital moment is present in cobalt square-planar compounds as well as in cobalt octahedral complexes. There are two points to be noted in the measurements of μ_{eff} in the CoPc polymorphs: (1) the temperature dependence of the magnetic susceptibility in α-CoPc is much less complicated than that in β-CoPc[20], and (2) the magnetic moment of β-CoPc at room temperature is about 15% higher than that of α-CoPc; consequently, the orbital contribution is larger.

The differences in the e.s.r. data are also seen in the values of the hyperfine constants A and B in the α- and β-phase. In the β-phase, A = 0.016 cm.$^{-1}$ and is smaller than B (0.028 cm.$^{-1}$). In going to the α-phase A diminishes by about one-third while B decreases by a factor of four and finally becomes smaller than A. An analysis of the equations[6,7] for A and B indicates that the change in B may be explained by the same decrease in Δ as mentioned above. However, this does not explain the variation in A with the present theory.[6]

The structural differences between the α- and β-phase are not only reflected in the e.s.r. spectra, but are responsible for a sharp difference in the electrical conductivity of the two polymorphs of H_2Pc. Wihksne and Newkirk[4] seem to imply that this difference in electrical conductivity is due to the contribution of paramagnetic centers which manifested themselves in a sharp e.s.r. line. This e.s.r. signal was found only in their α-sample. Actually we have observed this sharp e.s.r. signal in both α- (thin evaporated films or precipitated powder from H_2SO_4 solutions) and β- (sublimed crystals) samples, and we have found that the signal is due to oxygen impurity.[18] On the other hand, that the difference in conductivity between α- and β-phases is not due to oxygen impurities is also borne out by conductivity experiments[7] on single crystals which were carried out in oxygen and vacuum ambients and gave changes of conductivity that are orders of magnitude less than those found by Wikhsne and Newkirk on a pressed block of powder.

The lack of a superhyperfine structure is consistent with the placing of the unpaired electron in the d_{z^2} orbital which is also supported by our e.s.r. data for solutions. The explanation of the sensitivity to environment, however, must await a careful X-ray analysis of α-phthalocyanine similar to that performed by Robertson[2a] on the β-phase. Finally, the approximations employed in the development of the theory for square-bonded cobalt are being re-examined in the light of the data presented here.

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