Solvent Effects on the Spin Resonance Spectra of Cobalt Phthalocyanine

Jacques M. Assour

Contribution from the RCA Laboratories, Princeton, New Jersey.
Received June 28, 1965

A study of solvent effects on the electronic structure of the square-bonded Co^{2+} ion in the phthalocyanine molecule has been carried out with several heterocyclic amines. One notable feature of the e.s.r. spectra is the superhyperfine structure arising from the magnetic interaction between the Co^{2+} unpaired electron and the out-of-plane solvating molecules. A significant result found from these spectra is the sensitivity of the cobalt bonding parameters to the electronegativity of the solvent. A qualitative comparison between the nitrogen-orbital bonding coefficient measured by e.s.r. and the calculated charge density at the nitrogen atom of the solvating molecules has shown agreement.

I. Introduction

Metal-free phthalocyanine and most of its divalent metallic derivatives such as those of V, Ni, Cu, and Zn have limited solubility in most solvents presently available except sulfuric acid. This drawback has, in the past, prevented complete kinetic and reaction mechanism studies on the phthalocyanine complexes. Another important study, which so far has not been applied to these organometallic chelates, is the investigation of solvent effects on the hyperfine coupling constants of the paramagnetic ions in electron spin resonance (e.s.r.) spectra.[1] The intimate relation between the experimental hyperfine coupling constants and the bonding strength of the molecular ligands has been discussed earlier.[1]

Recently, during our investigations of the electronic and magnetic properties of phthalocyanines, cobalt phthalocyanine (abbreviated CoPc) has been found to be unusually soluble in several heterocyclic amine solvents when compared with other phthalocyanine derivatives. The increased solubility of CoPc in certain amines, together with the observed sensitivity of the molecular bonding orbitals of the Co^{2+} ion to axial crystal-field distortions,[2] led us to examine the effect of the solvating molecules on the bonding properties of the CoPc molecule.

This report presents a preliminary account of an e.s.r. investigation of solvent effects on the electronic structure of the Co^{2+} ion in phthalocyanine. The experiments reported here were performed using a group of heterocyclic amines, which have been selected with special emphasis on the electronegativity and steric effects associated with the environment of the nitrogen atom of the solvating molecule. The superhyperfine structures arising from the magnetic interaction between the Co^{2+} unpaired electron and extra out-of-plane nitrogen atoms have revealed interesting results on the out-of-plane bonding properties of the cobalt phthalocyanine molecule.

II. Experimental Results

The structure of the CoPc molecule is square-planar, as confirmed by X-ray analysis.[3] The cobalt atom is coordinated to four isoindole nitrogen atoms arranged in a square. The physical arrangement of the constituent atoms in the phthalocyanine molecule has been thoroughly described by Robertson.[3a]

The e.s.r. spectra described below were measured at liquid nitrogen (77°K.) temperature because at room temperature the resonance absorptions were not detected. A Varian spectrometer Model V-4500 employing 100-Kc. modulation was used. Spectra recorded for solutions in which the molar concentration was increased from 7×10^{-3} to 10^{-2} M did not show an appreciable variation in the resonance line width or separation between the hyperfine lines. The spectrum of each solution, except that in sulfuric acid, displayed nitrogen superhyperfine (shf) structure in addition to the cobalt hyperfine (hf) lines. At 77°K., the solutions under investigation become frozen and experimentally they behave as glassy media. Therefore, according to the method of Sands,[4] if the symmetry of the local field surrounding the Co^{2+} ion in solutions is tetragonal, one would observe the hyperfine structures associated with $g_{||}$ and $g_{\perp}$. Our spectra show that only the hf structure corresponding to $g_{||}$ is clearly resolved in all solutions. The hf structure associated with $g_{\perp}$ is quite complicated, and in most cases is not sufficiently resolved to allow accurate determination of the spin-Hamiltonian parameters. Table I summarizes the pertinent data derived from the spectra.

a. Sulfuric Acid. The spectrum shown in Figure 1 is composed of one intense resonance line flanked on the right by a set of eight peaks, and on the left by a set of five weak but visible peaks. The high-field lines are equally spaced with a separation $\Delta H = 89$ gauss. This hf structure is due to the nuclear magnetic interaction between the Co^{2+} unpaired electron and the cobalt nucleus of spin $I = \frac{7}{2}$ when the applied magnetic field is parallel to the magnetic axis of the molecule.[1c] The high-field hf structure including the intense resonance line is identical with that observed by Vanngard and Aasa.[5]

In order to observe the total low-field structure, the signal was amplified ten times while the modulation

(1) (a) R. Neiman and D. Kivelson, *J. Chem. Phys.*, **35**, 149, 156, 162 (1961); (b) E. M. Roberts and W. S. Koski, *J. Am. Chem. Soc.*, **83**, 1965 (1961); (c) S. E. Harrison and J. M. Assour, *J. Chem. Phys.*, **40**, 365 (1964); (d) J. M. Assour, J. Goldmacher, and S. E. Harrison, *ibid.*, **43**, 159 (1965).
(2) J. M. Assour and W. K. Kahn, *J. Am. Chem. Soc.*, **87**, 207 (1965).

(3) (a) J. M. Robertson, "Organic Crystals and Molecules," Cornell University Press, New York, N. Y., 1953; (b) M. A. Porai-Koshits, *Tr. Inst. Kristallogr. Akad. Nauk USSR*, **10**, 117 (1954).
(4) R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).
(5) T. Vanngard and R. Aasa, "Paramagnetic Resonance II," W. Low, Ed., Academic Press Inc., New York, N. Y., 1963.

Table I. Summary of Experimental Results for Frozen Solutions

Solution	$g_\perp$	$g_{\parallel}$	$10^4 B_{Co}$, cm.$^{-1}$	$10^4 A_{Co}$, cm.$^{-1}$	$10^4 B_N$, cm.$^{-1}$	$10^4 A_N$, cm.$^{-1}$
Sulfuric acid	2.546	2.029	96	85	...	...
Pyridine	2.268	2.016	a	78	12.8	11.4
Pyridazine	2.308	2.018	a	78	a	16.2
Isoquinoline	2.336	2.011	a	84	a	13.3
Quinoline	2.288	2.013	a	79	a	15.2
3-Methylpyridine	2.326	2.010	a	88	a	15.1
4-Methylpyridine	2.306	2.010	a	84	a	16.1
2-Methylquinoline	2.317	2.007	a	91	a	16.1

^{a} Unresolved.

amplitude was kept constant. The five visible peaks are equally spaced with $\Delta H = 80$ gauss. This structure is apparently different from that observed by Vanngard and Aasa, since these workers were unable to explain their spectrum in detail. The intense line is interpreted as a superposition of a number of hf lines corresponding to the cobalt nuclear transitions $M_I = -{}^3/_2, -{}^5/_2$, and $-{}^7/_2$ which belong to $g_\perp$.
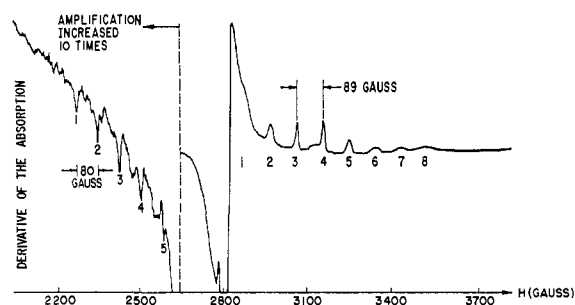

Figure 1. E.s.r. of 0.01 M cobalt phthalocyanine solution in sulfuric acid (77 °K.).

b. Pyridine. The spectrum of CoPc dissolved in pyridine displayed the high-field structure of the Co^{2+} ion as well as a complicated low-field structure. The cobalt high-field hf lines, however, were split each into five shf lines owing to the magnetic interaction between the 3d electron and extra out-of-plane molecular nitrogen atoms. In the pyridine solution, each solvating molecule has one nitrogen atom possessing a pair of nonbonding electrons which are located in an sp^2 σ orbital. This orbital is of the correct symmetry to interact with the $d_{3z^2-r^2}$ orbital of the cobalt ion. Since two out-of-plane nitrogen atoms can interact with the unpaired electron, one would therefore expect each Co^{2+} hf component to be split into five nitrogen shf lines, as observed in the e.s.r. spectrum of CoPc in pyridine.

c. Pyridazine and Pyrazine. To confirm the identification of the observed extra shf structure as that due to the magnetic interaction between the 3d electron and the nitrogen atoms of the solvating molecule, an effort was made to dissolve CoPc in pyrazine and pyridazine. These solvent molecules each contain two nitrogen atoms, and, consequently, one would expect to observe nine shf lines in the spectra of these solutions. In pyrazine, CoPc was not soluble, probably because the solvent has no dipole moment. In this molecule, the two nitrogen atoms are symmetrically located in the 1- and 4-positions of the heterocyclic ring, a result

leading to zero net electric dipole moment. On the hand, in the pyridazine molecule the two nitrogen atoms are asymmetrically located in the 1- and 2-positions, and therefore there is a net electric dipole moment. Indeed CoPc was found to be highly soluble in pyridazine.

The spectrum shown in Figure 2 for CoPc dissolved in pyridazine is typical of those recorded for CoPc dissolved in heterocyclic amines. In this spectrum, however, the cobalt hf components are each split into nine nitrogen shf lines. The cobalt component, $M_I = +{}^1/_2$, shown in the figure has been amplified to resolve the nine nitrogen lines. Their separation is about 17 gauss, and their intensities can be approximated by the expected ratio 1:4:10:16:19:16:10:4:1. This result leads to two significant conclusions: (1) the extra shf structure originates from the nuclear interaction between the unpaired electron of the cobalt ion and the *nitrogen atoms of the solvating molecules;* (2) the two nitrogen atoms in the pyridazine molecule are equally coupled to the unpaired electron.
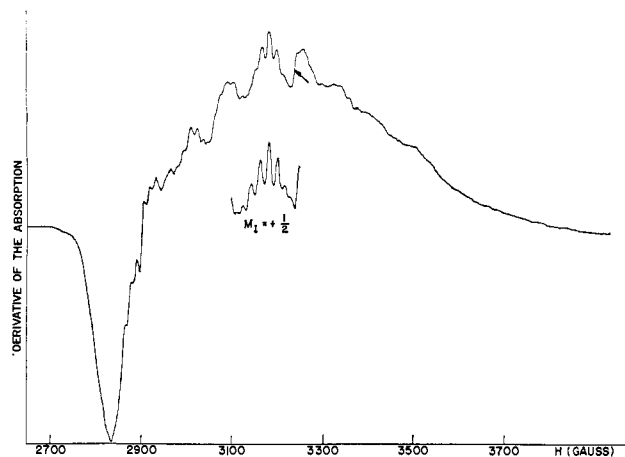

Figure 2. E.s.r. of cobalt phthalocyanine solution in pyridazine (77 °K.).

The arrow marked in Figure 2 indicates the location of one narrow resonance line which has also been observed in the spectra of other solutions. This narrow line is located at about $H = 3244$ gauss, and its g value in all solutions is $g = 2.0034$. We believe that this line is due to the free-radical resonance observed earlier in polycrystalline samples.[2] The correlation of the single sharp resonance in the frozen solutions and solids suggests that in the former there are small undissolved phthalocyanine particles that have been able to absorb oxygen.
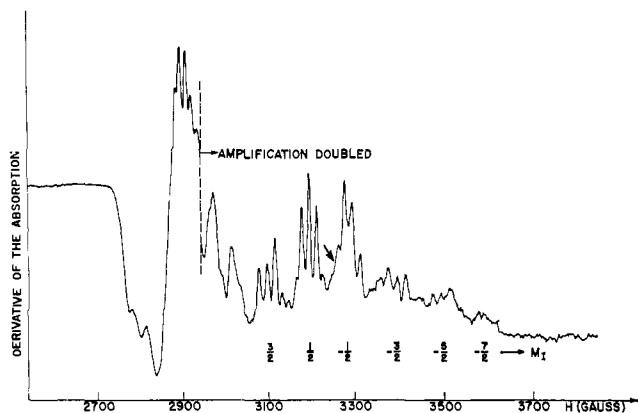
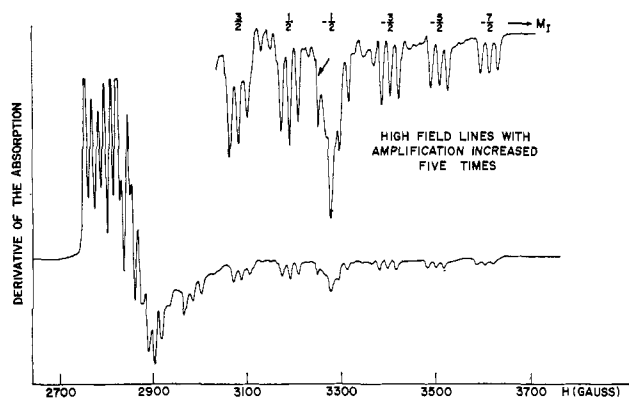Figure 3. E.s.r. of cobalt phthalocyanine solution in quinoline (77°K.).

Figure 4. E.s.r. of cobalt phthalocyanine solution in 4-methylpyridine (77°K.).

Figure 5. E.s.r. of cobalt phthalocyanine solution in 2-methylquinoline (77°K.).

d. Isoquinoline and Quinoline. The nearest neighbors of the nitrogen atom in isoquinoline are identical with those present in pyridine and the resultant magnetic interactions in both solvents is therefore expected to be approximately the same. Although the resonance spectrum of the isoquinoline solution was found to be similar to that of the pyridine solution, the spin-Hamiltonian parameters (Table I) obtained from the two spectra are different. These variations are discussed later.

The spectrum recorded for a quinoline solution is shown in Figure 3. The high-field cobalt lines are well resolved and each is split into five shf lines, as expected. Note that the intensities of the nitrogen lines associated with the cobalt component, $M_I = \frac{1}{2}$, are given approximately by the ratio $1:2:3:2:1$. Also, as indiated by the arrow, the free-radical resonance is observed in this spectrum.

e. 2-Methyl-, 3-Methyl-, and 4-Methylpyridine. The heterocyclic amine solvents discussed thus far contain one or two nitrogen atoms whose nonbonding orbitals interact with the Co^{2+} unpaired electron. The hyperfine coupling constants characteristic of this interaction have been shown to vary with solvent and, as evident from the data, they are dependent on the electronegativity of the out-of-plane nitrogen atoms. In order to examine this dependence more closely, electron-donating groups were substituted for one hydrogen atom in the pyridine molecule in the *ortho*, *meta*, and *para* positions. Since nitrogen is the most electronegative atom in the pyridine molecule, it will accept a large portion of the charge density contributed by the donor group. The increase in charge density on the nitrogen atom is directly related to the bonding strength of its orbitals.

In 2-methylpyridine, CoPc was found to be insoluble. However, in 3-methyl- and 4-methylpyridine the solubility of CoPc appeared by visual comparison to be higher than that in pyridine. These solutions gave well-resolved spectra as shown in Figure 4 for CoPc dissolved in 4-methylpyridine. The high-field resonance structure is characteristic of both the cobalt and nitrogen hyperfine interactions. The low-field structure is unfortunately quite complicated due to strong overlap between the cobalt lines.

f. 2-Methylquinoline. The insolubility of CoPc in 2-methylpyridine is rather surprising considering the fact that the methyl group is close to the nitrogen atom in the ring, and a considerable increase in the electronegativity of the nitrogen atom is expected. On the other hand, CoPc was found to be soluble in 2-methylquinoline. As shown in Figure 5, the high-field resonance structure is sufficiently resolved to allow the observation of the cobalt hf and the nitrogen shf lines. The free-radical resonance is also detectable.
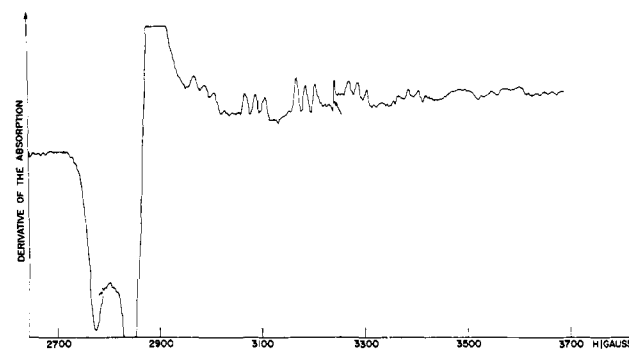
III. Discussion

The sensitivity of the hyperfine coupling constants of the Co^{2+} ion to the nature of the heterocyclic amines, and the direct observation of the superhyperfine structure of the out-of-plane nitrogen atoms unequivocally confirm the assignment of the unpaired electron to the $d_{3z^2-r^2}$ level of the Co^{2+} ion. This assignment can be rationalized as follows. The local ligand field acting on the Co^{2+} ion splits the five orbitally degenerate 3d levels into three singlet levels $d_{x^2-y^2}$, $d_{3z^2-r^2}$, d_{xy}, and a doublet level composed of the d_{xz} and d_{yz} levels. After accommodating the seven 3d electrons with their spins paired in the four 3d levels, one electron remains unpaired. The e.s.r. spectra resulting from the magnetic interaction between this electron and the neighboring atomic nuclei are critically dependent on the ground state of the Co^{2+} ion. First, that the unpaired electron is not located in the $d_{x^2-y^2}$ orbital is clearly evident from the spectra, because no shf structure typical of the in-plane pyrrole nitrogens has been found as was the case with copper phthalocyanine.[1a-c] Second, that the 3d electron is unlikely to be located in the doublet level can be readily established by comparing

the theoretical values of the spin-Hamiltonian parameters with the experimental data. Third, the d_{xy} orbital is oriented in the plane of the phthalocyanine molecule and has nodes both at the cobalt nucleus and at the pyrrole nitrogens. Because this orbital is capable of combining with only in-plane π-orbitals, it is hardly possible for the d_{xy} orbital to overlap with σ-orbitals of ligands oriented along the axial positions. In vanadyl phthalocyanine,[1d] the d_{xy} orbital containing the V^{4+} unpaired electron has been found to be completely localized on the vanadium atom, and no shf structure due to the neighboring nitrogens was detected. Furthermore, the variations of the g factors and hyperfine splitting constants obtained for CoPc in the solid state and in solutions are inconsistent with those determined for $(VO)^{2+}$ complexes. In these compounds, the d_{xy} orbital is concentrated mainly in the molecular plane and it is slightly perturbed by the electrostatic field of extra out-of-plane ligands. Therefore, it is concluded that the d_{xy} orbital does not contain the Co^{2+} unpaired electron.

The $d_{3z^2-r^2}$ orbital is, on the other hand, perpendicularly oriented along the molecular fourfold symmetry axis, and therefore, is capable of interacting with σ orbitals of out-of-plane nitrogen atoms. These σ orbitals are sp^2-hybridized orbitals which contain a finite s-electron density at the bonding nitrogen atoms, and thus conveniently explain the shf structure observed in our spectra. Although a portion[6] of the $d_{3z^2-r^2}$ orbital lies in the xy molecular plane and has the possibility of overlapping with the σ orbitals of the pyrrole nitrogen atoms, such interaction has not been observed in our experiments with solutions or solids. Hence, the $d_{3z^2-r^2}$ orbital has most of the properties necessary to explain our experimental observations, and these observations are in agreement with our interpretation of the extra superhyperfine structure.

The variations of the hyperfine coupling constants and the spectroscopic g factors, summarized in Table I, are indicative of a strong magnetic interaction between the solvent and solute. The data listed in Table I are the average of measurements made on three samples. In all solutions, $g_{||}$ is close to the free-electron value in fair agreement with theory, whereas $g_{\perp}$ is reduced considerably from that measured for single crystals.[2] Moreover, for all the heterocyclic amines solutions, $g_{\perp}$ is found to be smaller than that measured for the α-CoPc polymorph.[2] Similar variations of the g factors in pyridine and quinoline solutions have been also reported by Griffith.[7] In solutions, A_{Co} is reduced by a factor of two from that in the crystal; however, it has no striking variations between solutions. In the sulfuric acid, B_{Co} has decreased by a factor of three in comparison to the value measured for single crystals.

The shf structures observed in solutions give direct information on the amount of charge transfer between the cobalt ion and the out-of-plane nitrogens. Using hydrogen-like wave functions for the atomic orbitals, the coupling energies describing the interaction of the 3d electron with the axial ligands are

$$E_{||} = \left(\frac{\epsilon_2}{\sqrt{2}}\right)^2 2\gamma_N \beta \beta_n \left[-\frac{8\pi}{9} \delta \underset{\rightarrow}{(r)} + \frac{8}{15}\langle r^{-3}\rangle_p \right] \quad (1)$$

$$E_{\perp} = \left(\frac{\epsilon_2}{\sqrt{2}}\right)^2 2\gamma_N \beta \beta_n \left[-\frac{8\pi}{9} \delta \underset{\rightarrow}{(r)} - \frac{1}{15}\langle r^{-3}\rangle_p \right] \quad (2)$$

The z axis has been chosen along the bond N–Co–N perpendicular to the molecular plane. $E_{||}$ and $E_{\perp}$ are the coupling energies parallel and perpendicular to the z axis. ϵ_2 is the nitrogen-orbital bonding coefficient of the ground-state molecular orbital of the complex, γ_N is the magnetic moment of the N^{14} nucleus, $\delta(r)$ corresponds to the s-electron density at the nitrogen nuclei, and $\langle r^{-3}\rangle_p$ is the expectation value for the 2p orbital of the nitrogen atom. β is the Bohr magneton and β_n is the nuclear magneton.

In order to present a meaningful discussion on the amount of covalent bonding in these complexes, the pyridine solution is discussed as an example with the understanding that the following analysis is applicable to all solutions. Maki and McGarvey[8] have calculated the nitrogen 2s function $\delta(r)$ and the expectation value $\langle r^{-3}\rangle_p$ using s.c.f. wave functions for the nitrogen atom. Substituting their values in eq. 1 and 2, along with the experimental shf splitting parameters (Table I) for the pyridine solution, we find $\epsilon_2 = 0.38$. This constant can be now used to calculate the bonding coefficient ϵ of the $d_{3z^2-r^2}$ atomic orbital.

The normalization condition of the ground-state molecular orbital is expressed by

$$\epsilon^2 + \epsilon_2^2 - 2\epsilon\epsilon_2 S_2 = 1 \quad (3)$$

where $S_2 = \langle d_{3z^2-r^2} | 2^{-1/2}(\sigma_5 - \sigma_6) \rangle$ is the overlap integral between the Co^{2+} atomic orbital and σ orbitals of the out-of-plane nitrogens. In-plane overlap integrals have been neglected.[6] A quantitative estimate of the overlap integral S_2 depends on the magnitude of the effective nuclear charges (Z) of the overlapping atomic orbitals and the internuclear distance between overlapping atoms. Although approximate values for the effective nuclear charges are readily available, direct measurements of the axial cobalt–nitrogen internuclear distance (R_2) in each CoPc–amine complex require an extensive X-ray analysis, which is outside the scope of the present work. However, in order to obtain a relative magnitude of the cobalt-orbital bonding coefficient in the pyridine complex, we have chosen $R_2 = 2.1$ Å. This internuclear distance is representative of the cobalt–nitrogen bond distances presently known. Using $Z(Co^{2+}; 3d) = 8.8$, $Z(N; 2s) = 4.5$, and $Z(N; 2p) = 3.5$, we find $S_2 = 0.14$. Inserting $\epsilon_2 = 0.38$ and $S_2 = 0.14$ in eq. 3, $\epsilon = 0.97$ is found. This result is quite reasonable.

The dependence of the nitrogen-orbital bonding coefficient on the electronegativity of the heterocyclic amines suggest an apparent relationship between the e.s.r. bonding parameters and the electronic charge density at the nitrogen atom of the solvating molecules. Furthermore, it is believed here that the perpendicularly oriented orbital of the unpaired electron in the planar CoPc molecule can be effectively used as a probe in

(6) Note that the relative overlapping power of the out-of-plane positive lobes of the $d_{3z^2-r^2}$ orbital is twice that of the in-plane negative lobe.

(7) J. S. Griffith, *Discussions Faraday Soc.*, **26**, 81 (1958).

(8) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958)

investigating several properties of heterocyclic amines. These molecules and their derivatives are commonly classified as π-deficient N-heteroaromatics. The nitrogen atom in each molecule has a considerable electron-attracting power such that it is able to withdraw π electrons from the organic ring, and consequently, causes a deficiency of π electrons on the surrounding carbon atoms in the aromatic ring. There is, however, one unique property common to all the heterocyclic amines; namely, each nitrogen atom has a pair of nonbonding electrons occupying a σ orbital. Although in e.s.r. experiments, the charge density contained in the nonbonding orbital is of major importance, the polarization of this orbital determines in large part its capability to overlap with the cobalt orbital and ultimately controls the amount of charge transfer between the bonding atoms. The polarization of the electronic orbitals is largely dependent on several factors such as inductive and field effects, resonance effects, and the steric environment of the nitrogen atom.

Presently, we know two properties of the solvating molecules which might be correlated with the e.s.r. results. The first is the basicity of these molecules measured in units of pK_a, and the second is the calculated π-charge densities at the nitrogen atoms. It seems appropriate, at this point, to ask first if any known relation exists between the measured base strength of a given molecule and the calculated charge density on its constituent atoms. Earlier correlations by Longuet-Higgins and Coulson[9] and by Brown and Dewar[10] have unfortunately shown that there is no simple relationship between these two quantities. Although Longuet-Higgins and Coulson[9] have further suggested a possible relationship between the basicity of the heterocyclic amines and their dipole moments, a comparison[10] of the calculated and measured dipole moments for these molecules proved to be unsatisfactory. Recently, however, a study[11] on the electronic structure of heterocyclic amines has shown a linear relationship between the basicity of the molecule and the charge density on the nitrogen atom. This relationship was obtained by adjusting the electronegativity parameter of the heteroatom in each molecule.

The experimental e.s.r. parameter most sensitive to the nature of the solvating molecule is the out-of-plane nitrogen-orbital bonding coefficient defined as ϵ_2. Quantitatively, $|\epsilon_2|^2$ is a measure of the covalent bonding between the cobalt atom and the out-of-plane nitrogens. The magnitude of $|\epsilon_2|^2$ is dependent on the internuclear distance (overlap between the cobalt and nitrogen orbitals) and charge density. For the cases under discussion, specifically for the pyridine molecule and its *meta-* and *para*-substituted derivatives, the internuclear distance is expected to remain constant and the only variable parameter is the charge density on the N-heteroatom. The same is expected to be true for other parent and monosubstituted molecules.

The first interesting feature of the experimental results is the apparent correlation between $|\epsilon_2|^2$ and the π-electron density at the nitrogen atom in pyridine,

isoquinoline, and quinoline.[12] The magnitude of $|\epsilon_2|^2$ found for the solvents pyridine, isoquinoline, and quinoline is of the order of 0.144, 0.168, and 0.193, respectively, while the calculated[9,10,13] π-electron densities for these molecules have shown that the charge density on the nitrogen atom increased in the following order: pyridine < isoquinoline < quinoline. The increase in charge density is thus in agreement with the increase in the bonding coefficient. A similar correspondence has been also found for the following group: pyridine < 3-methylpyridine < 4-methylpyridine. On the other hand, an attempt to compare the magnitude of $|\epsilon_2|^2$ to the measured[14] basicity of the above solvents has shown a complete inconsistency.

In pyridine and the *para* and *meta* methyl-substituted derivatives, $|\epsilon_2|^2$ increased from 0.144 in pyridine to 0.193 in 3-methylpyridine and 0.202 in 4-methylpyridine. The progressive increase of $|\epsilon_2|^2$ is consistent with the relationship of increased charge density at the bonding site owing to the donating power of the methyl group and less steric interference as the substituent is further removed from the bonding site. The experimental fact that the solubility of CoPc in 2-methylpyridine is extremely low, although the charge density at the nitrogen atom is greater than that in 3-methylpyridine, can be explained in terms of a strong steric interference due to the *o*-methyl group. On the other hand, we have observed weak but easily detectable e.s.r. signals of CoPc dissolved in 2-methoxypyridine and 2-chloropyridine. The substituents in these molecules are in the *ortho* positions, but they differ in their electron-donating power. The methoxy and chlorine groups are known to contribute to the base weakening of the solvents through their inductive effects, but they have a lease-strengthening contribution due to resonance effects. Presently, the chemical and physical properties of the *ortho* substituents and their influence on the bonding strength of the pyridine molecule are not completely understood and are in need of further exploration.

One puzzling experimental result was the fact that CoPc was found to be sufficiently soluble in 2,6-dimethylpyridine to allow the detection of weak e.s.r. signals which were readily identified as those characteristic of the hyperfine structures of both the Co^{2+} ion and the nitrogen atoms of the solvating molecule. This result is rather confusing since one would expect that in 2,6-dimethylpyridine the steric interactions of the two methyl groups flanking the nitrogen atom should be much stronger than those in 2-methylpyridine. It is interesting to note, however, that studies[15] on the affinity of substituted pyridines towards iron(II) porphyrin have shown the same phenomenon; namely, the solvent 2,6-dimethylpyridine has a greater affinity than 2-methylpyridine. According to Falk,[15] this effect can be explained by assuming that the lengthened perpendicular bond in the former molecule is more

(12) It should be noted that ϵ_2 is a measure of the σ-bonding between the cobalt orbital and the nonbonding orbital of the out-of-plane nitrogen atoms. The latter orbital has been assumed to be localized in the plane of the solvating molecule and presumably does not couple with the π-electron system. However, the charge density in the nonbonding orbital is proportional to the total charge on the nitrogen atom.

(9) H. C. Longuet-Higgins and C. A. Coulson, *J. Chem. Soc.*, 971 (1949).

(10) D. A. Brown and M. J. S. Dewar, *ibid.*, 2406 (1953).

(11) M. Iwaizumi, *J. Chem. Soc. Japan*, 82, 306 (1961).

(13) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, 43, 87 (1947).

(14) E. F. G. Herrington, *Discussions Faraday Soc.*, 9, 26 (1950).

(15) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964.

stable than the tilted bond in 2-methylpyridine. This simple interpretation by Falk for the spatial mobility of the nonbonding orbitals in these two solvents, and, in fact, in any heterocyclic amine molecule, is yet to be substantiated by additional quantitative evidence.

IV. Summary

Studies of solvent effects on the electronic structure on the square-bonded Co^{2+} ion in the phthalocyanine molecule have been performed with several heterocyclic amine solvents and their substituted derivatives. The most notable feature of the e.s.r. spectra is the superhyperfine structure arising from the magnetic interaction between the Co^{2+} unpaired electron and out-of-plane nitrogen atoms of the solvating molecules. A qualitative comparison between the e.s.r. nitrogen-orbital bonding coefficient and the calculated charge density at the out-of-plane nitrogen atoms has shown agreement. Additional investigations with substituted pyridine solutions are under way to determine a relationship between the e.s.r. bonding coefficients, π-electron densities, and basicity of these molecules.

Chelate Chemistry. III.[1] Chelates of High Coordination Number
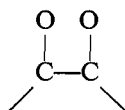
E. L. Muetterties and C. M. Wright

Synthesis, properties, and structural interpretations are presented for seven- and eight-coordinate structures based on the tropolone anion and the following elements: scandium, yttrium, titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, rare earth metals, indium, tin, and lead. Oxygen atoms in the chelated tropolone anion apparently are three-coordinate in the tris chelates of some rare earth metals and yttrium but not in scandium, titanium, iron, and rhodium.

Introduction

In the first paper[2] of this series, an argument was presented that the tropolone anion, T, is ideally suited to

T
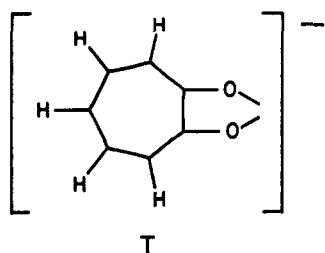
the formation of structures of high coordination number by virtue of the planarity and compactness of the ligand and the rigidity of the

functionality. Seven- and eight-coordinate structures were described for the tropolone anion with indium, tin, and lead. A more detailed assay of high coordination structures based on tropolone is the subject of this paper.

Group III Tetrakis Chelates. The tristropolonates of scandium, yttrium, and the rare earth trivalent ions react with sodium tropolonate in polar media to form sodium salts of the respective metal tetrakistropolonate anions, $Na^+MT_4^-$. These salts are analogous to the earlier described[2] indium compound, $Na^+InT_4^-$.

There appears to be a real structural identity among all these tetrakistropolonates. Firstly, the infrared spectra of the crystalline salts are simple and strikingly similar. Secondly, and more definitively, the lattices are isomorphous by X-ray powder diffraction criterion. Because eight-coordination is a well-established phenomenon for rare earth ions such as europium, and because of the spectral and diffraction similarities of the solid lattices, we believe that these chelates are eight-coordinate in the solid state. Owing to the low solubility of the diamagnetic salts, no spectral information relevant to the solution state was obtained. However, the proton n.m.r. spectra of the paramagnetic salts displayed pseudo-contact shifts significantly different from the tris chelates. For example, $(CD_3)_2SO$ solutions of $Na^+PrT_4^-$ showed broad proton resonances at -8.7 and -10 p.p.m. compared to -10, -11.7, and -13.3 p.p.m. for PrT_3 in $(CD_3)_2SO$. These large diamagnetic shifts for PrT_4^- relative to PrT_3 suggest that there is no gross dissociation of PrT_4^- in solution. There is, however, ligand exchange between tropolone and PrT_4^- in $(CD_3)_2SO$ solutions as judged by the averaging in the proton n.m.r. spectra of such mixtures.

An isomorphous group of acids, $H^+RT_4^-$, and an isomorphous group of ammonium salts, $NH_4^+RT_4^-$, were also prepared and characterized.

Attempts were made to extend this chemistry to other trivalent ions. We obtained no evidence of

(1) Paper II: E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, **87**, 21 (1965).

(2) E. L. Muetterties and C. M. Wright, *ibid.*, **86**, 5132 (1964).