than the Co–Ge bond,[26] and that the Co–M bond strengths vary significantly (twofold or more) with changes in electronegativity of other atoms (X) to which the metals are bound. The latter conclusion will be of particular interest in extending this model work on discrete metal–metal bonded molecules to the study of intermetallic forces in dilute alloys.

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[26] It has been suggested by a reviewer that, in addition to the data and correlations concerning Co–Sn and Co–Ge π bonding, the greater Co–Sn π bonding can be rationalized in terms of greater X–M π bonding in the case of Ge as opposed to Sn, which could reduce the amount of effective Co–Ge π bonding with respect to Co–Sn π bonding.

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Electron Spin Resonance Studies of Low-Spin Cobalt(II) Complexes. Base Adducts of Cobalt Phthalocyanine

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The effects of the extraplanar ligands DMSO, pyridine, imidazole, and cyanide on the esr spectra of cobalt complexes of tetrasulfonated phthalocyanine have been studied. With the first three ligands, a marked change in the esr spin-Hamiltonian parameters was observed with increasing basicity. In the case of cyanide, the Co(II) species was found to be no longer stable. Evidence is presented for an "intramolecular" oxidation–reduction reaction to a Co(III) complex of the phthalocyanine anion. Efforts to prepare simple 1:1 oxygen adducts of these complexes were unsuccessful.

Introduction

Considerable recent work has been devoted to the reactions of a group of low-spin cobalt(II) complexes, many of which form cobalt hydrides, organocobalt complexes, oxygen adducts, and peroxo-bridged dimers under suitable conditions. Included in this group are vitamin B_{12r}, bis(dimethylglyoximato)cobalt, cobalt porphyrins, and cobalt phthalocyanines (CoPc). The reactions of all of these complexes are strongly influenced by extraplanar ligands, as has been shown in a comparison of B_{12r} and cobaloxime chemistry.[3]

Since the unpaired electron in these complexes is in a d_{z^2} orbital, the orbital directly involved in the coordination of extraplanar ligands, electron spin resonance (esr) provides a particularly sensitive tool for the study of these species. Thus, esr spectra provided strong evidence for the coordination of the 5,6-dimethylbenzimidazole "fifth ligand" to the central cobalt in vitamin B_{12r}.[4–6] Addition of either pyridine or imidazole had no effect on the spectra, indicating the absence of further sixth-position coordination by the free base. This behavior is in contrast to that of cobaloximes, of cobalt phthalocyanines,[7] and of derivatives of cobalt tetraphenylporphine (CoTPP),[8] which readily form six-coordinate bis-pyridine complexes. With imidazoles, however, only the monoadducts (of the cobaloximes and porphines) are formed. Esr studies of the coordination of imidazoles with CoPc have not been reported.

In the presence of air, many of these complexes reversibly form 1:1 adducts with molecular oxygen, and pronounced changes in the esr spectra are observed.[8–12] The equilibrium constants and reversibility of this adduct formation and the tendency toward further reaction to the peroxo-bridged dimers are functions both of the extraplanar ligand and of the specific cobalt complex. Increasingly basic ligands, for example, favor formation of the oxygen adduct.[8]

In an effort to elucidate the effect of axial ligands on the electronic structure of these B_{12} models and, hopefully, their oxygen adducts, we have undertaken an esr study of the base adducts of tetrasulfonated cobalt(II) phthalocyanine, Na_4CoPTS. In view of the earlier work cited above, the ligands pyridine, imidazole, and cyanide were chosen. Studies of sulfonated phthalocyanines in aqueous solution can be complicated by molecular association.[13] For this reason, dimethyl sulfoxide (DMSO) was used; in this solvent, association has been shown to be absent.[14]

The unambiguous interpretation of paramagnetic resonance spectra of polycrystalline or frozen-glass samples at a single frequency can be difficult or im-

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[1] Contribution No. 4168.

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TABLE I

ESR DATA FOR $Na_4CoPTS \cdot nL$ IN DMSO AT 77°K

n	L	$g_{\parallel}$	A_{Co}	A_N	$g_{\perp}$	B_{Co}	B_N	Q'
2	DMSO	2.005	(+)0.0098[a]	. . .	2.257	(−)0.0021	. . .	(+)0.0002
			±0.0002					±0.0001
1	Pyridine	2.005	(+)0.0086	0.0015	2.220	(−)0.0031	[b]	[b]
1	Imidazole	2.005	(+)0.0080	0.0017	2.220	(−)0.0031	[b]	[b]
			±0.0004	±0.0001				
2	Pyridine	2.006	(+)0.0076	0.00140	2.174	(−)0.0052	0.0012[a]	[b]
2	Imidazole	2.007	(+)0.0067	0.00150	2.155	(−)0.0067	0.0014	[b]
		±0.002	±0.0002	±0.00005	±0.005	±0.0005	±0.0001	

[a] All nuclear hyperfine coupling constants and quadrupole coupling constants are expressed in cm^{-1}. [b] Could not be determined.

possible due to the combined effects of hyperfine interaction, nuclear electric quadrupole interactions, rhombic distortions of the complex, and "anomalous" absorptions. The application of high-frequency esr instrumentation and the use of a second-order theory for the analysis of polycrystalline line shapes, described in one of our earlier papers,[15] have now made it possible to extract reliable spin-Hamiltonian parameters from such spectra. These techniques have been used in the present work.

Experimental Section

Materials.—The preparation and purification of Na_4CoPTS have been described earlier.[14] DMSO, pyridine, and NaCN were all of reagent quality. Karl Fischer titration showed the water content of the DMSO to be *ca.* 10^{-2} *M*. No changes in the results were observed when DMSO, dried by fractional distillation from CaH_2 under vacuum, was used. Imidazole (Matheson Coleman and Bell, mp 89–91°) was used without further purification.

Method.—Samples were prepared under nitrogen from the appropriate quantities of DMSO solutions of the individual species, all well deoxygenated before mixing. Concentrations ranged from about 0.03 to 0.08 *M* Na_4CoPTS. The resulting solutions were transferred under nitrogen to quartz tubes, sealed, and frozen by immersion in liquid nitrogen. For studies of the products of reaction with molecular oxygen, the samples were returned to room temperature and bubbled with oxygen for varying lengths of time. Subsequent deoxygenation with nitrogen or helium did not affect the results.

Details of the esr instrumentation as well as a complete discussion of the computer program used in analyzing the spectra have been given in our earlier paper.[15] In the investigations at K band (ν = 34.80 kMc) thin-walled quartz sample tubes of 1–2-mm diameter were employed. Larger tubes (2–3 mm) were used at X band (ν = 9.535 kMc). Visible spectra were obtained on a Cary Model 14 spectrophotometer with 0.1- and 1-mm cells.

Results

Frozen DMSO solutions of $Na_4CoPTS \cdot 2L$, where L = DMSO, pyridine, and imidazole, were investigated at 77°K. Table I summarizes the esr results obtained. In the absence of base, the species present in solution was assumed to be $Na_4CoPTS \cdot 2DMSO$. It is felt, however, that these esr experiments cannot differentiate between a five- and six-coordinate DMSO complex.

In Table I, the symbols $g_{\parallel}$ and $g_{\perp}$ designate values of the g tensor when the symmetry axis (z axis) of the molecule is aligned parallel and perpendicular to the magnetic field, respectively; A and B denote the corresponding values of the nuclear hyperfine interaction constants. Since the nitrogen atoms giving rise to the superhyperfine splitting lie along the symmetry axis, A_N and B_N are analogous to A and B and denote the ligand hyperfine interaction constants when the magnetic field is parallel to and perpendicular to the z axis, respectively. Where quadrupole interaction of the transition metal could be shown to contribute to the esr spectrum, a value of Q', the nuclear electric quadrupole interaction constant, has also been given.

$Na_4CoPTS \cdot 2L$ (L = DMSO, py, Imidazole).—Figures 1 (X band) and 2 (K band) show the spectral changes in the esr spectrum of the cobalt complex observed on addition of the ligands pyridine and imidazole. The marker near 3400 G in Figure 1 indicates the position of the diphenylpicrylhydrazyl (DPPH) standard.

Solutions were prepared with ligand:Na_4CoPTS ratios of 0.5, 1.0, 1.5, 2.0, 5.0, and 10.0. At ratios of 1:1 and 2:1 the spectra indicated that the species present were essentially $Na_4CoPTS \cdot$(base) and $Na_4CoPTS \cdot 2$(base), respectively. In the 2:1 case, the five superhyperfine components expected for $Na_4CoPTS \cdot 2$(base) were observed to be at least partially resolved. In the case of the 1:1 complexes only three superhyperfine components wereob served. As indicated in Table I the uncertainties in the data obtained for these 1:1 complexes are somewhat greater than those obtained for the better defined 2:1 analogs. The spectra of the 1:1 complexes did not, however, appear to be superpositions of the $Na_4CoPTS \cdot 2DMSO$ and the $Na_4CoPTS \cdot 2$(base) signals.

At X band (Figure 1) the addition of extraplanar nitrogen donors yielded an apparent complication of the spectra. This results from overlapping of the parallel and perpendicular resonance envelopes. In the absence of base, the signal resulting from molecules whose symmetry axes are principally oriented perpendicular to the direction of the field is localized near 2800 G. Addition of two pyridines to give $Na_4CoPTS \cdot 2py$ caused a marked increase in B and a significant reduction in $g_{\perp}$ shifting $H_{\perp}°$ to about 3150 G. A slight decrease in $H_{\parallel}°$ was also observed, but here the most notable effect was the decrease in the A value. In the spectra of the imidazole complex, these effects were even more pronounced. The greater line width in the parallel components in the presence of base is probably the result of unresolved nitrogen superhyperfine structure.

The spin-Hamiltonian parameters obtained from X-band spectra were confirmed by the studies at K band (Figure 2). The greater spectrometer sensitivity at K band and the advantages of the higher field and frequency in separating and clarifying the parallel and perpendicular signals are obvious upon a comparison of Figures 1 and 2. In the parallel spectra, the decrease in A and the appearance of ligand hyperfine structure are most apparent. The anomalous signal near 12,400 G in the $Na_4CoPTS \cdot 2imid$ spectrum is the result of a small amount of oxygen in the sample, as discussed below. The spectral regions at lower field clearly reveal the decrease in $g_{\perp}$ in the series L = DMSO, py,

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[15] L. D. Rollmann and S. I. Chan, *J. Chem. Phys.*, **50**, 3416 (1969).

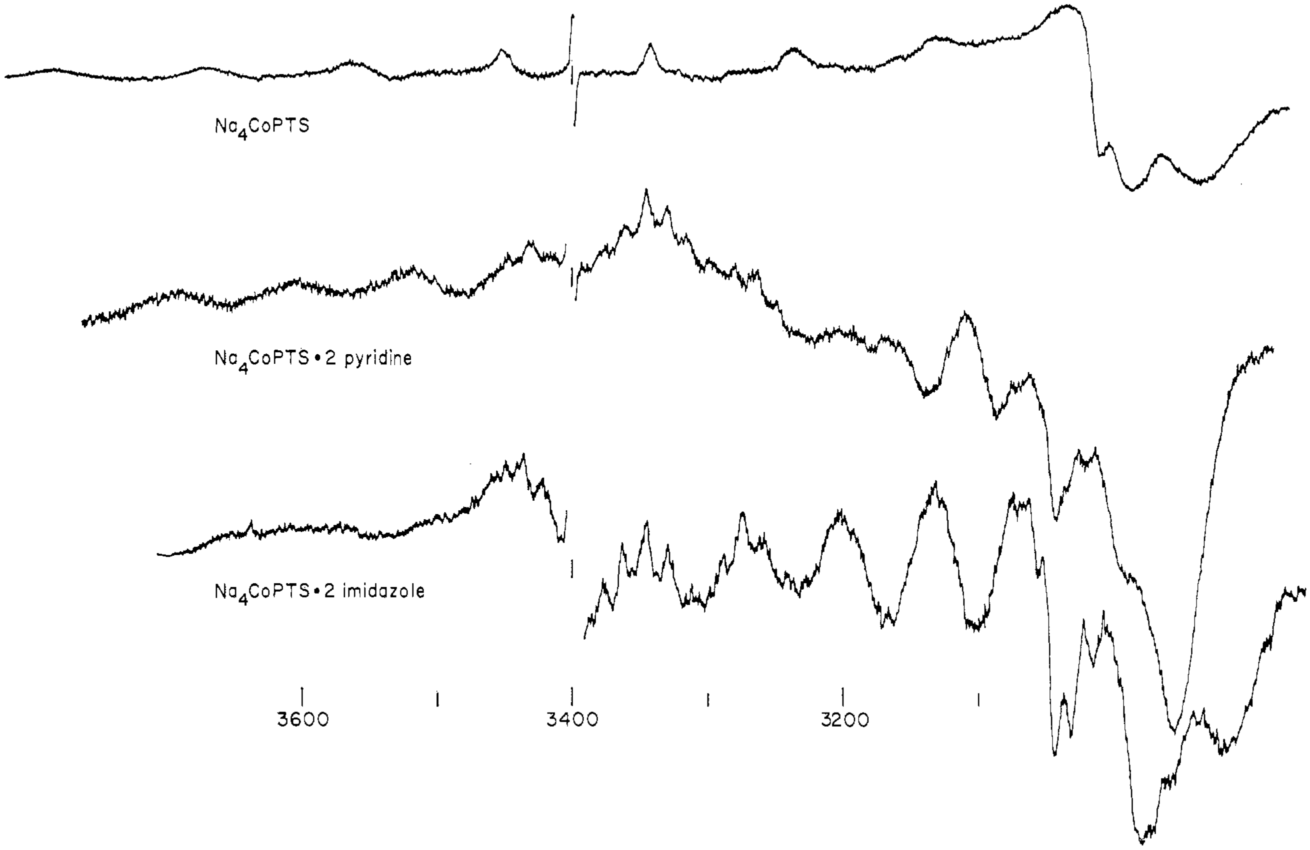

Figure 1.—X-band esr spectra of base adducts of Na_4CoPTS in DMSO at 77°K.

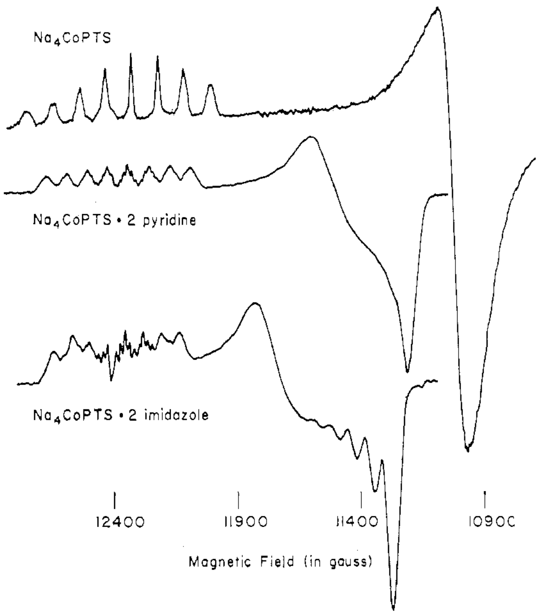

Figure 2.—K-band esr spectra of base adducts of Na_4CoPTS in DMSO at 77°K.

imid, but only in the case of the imidazole complex was the hyperfine structure about $H_\perp{}^\circ$ resolved. None of the K-band spectra exhibited ligand hyperfine structure in this region.

Reactions with O_2.—In an attempt to identify adducts of the type L–Na_4CoPTS–O_2, solutions of the various complexes were treated with molecular oxygen. No change in the esr spectra of the complexes $Na_4CoPTS\cdot2L$, where L = DMSO and py, was observed. The imidazole complex, however, reacted rapidly and irreversibly. This reaction process has been followed by esr and the results are shown in Figure 3. At least two and probably three paramagnetic species were indicated.

Brief exposure to oxygen yielded a transient signal at $g = 1.984$ (Figure 3A), the peak disappearing on further oxidation. The oxygen-insensitive portion of the spectrum showed a resonance at $g = 2.040$ ($A = 16$ G) and a very intense signal near the free-electron

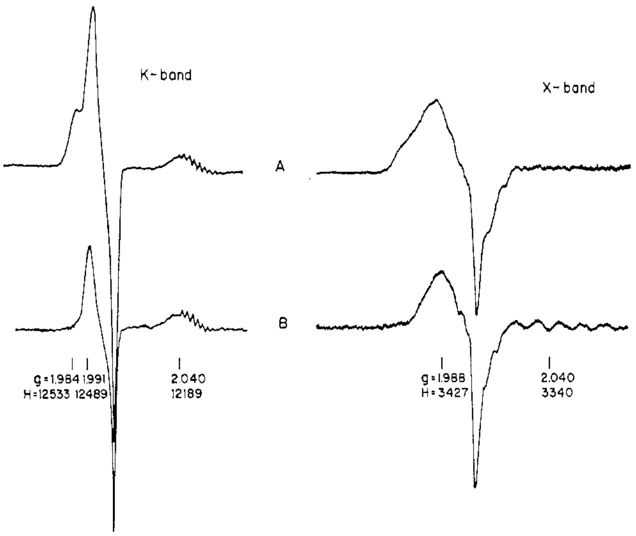

Figure 3.—X- and K-band esr spectra of the reaction products of the Na_4CoPTS–imidazole complexes with molecular oxygen in DMSO at 77°K: (A) spectrum of initial oxidation product; (B) spectrum after exhaustive oxidation.

value. The relative intensities of these two signals were not, however, constant among various samples, and it is thought that two different species are present in these frozen glasses. No change was observed in the visible spectra of these solutions on exposure to oxygen, evidence suggesting that the radicals formed do not involve the phthalocyanine π system.

$Na_4CoPTS \cdot 2NaCN$.—Addition of carefully deoxygenated DMSO solutions of NaCN to those of Na_4-CoPTS, under nitrogen, yielded the spectra shown in Figure 4. Expansion of the K-band signal about $H° =$ 12463 G showed the presence of hyperfine structure similar to, but less pronounced than, that observed at X band. Identical spectra were observed when the isotopically labeled compounds $Na^{13}CN$ and $KC^{15}N$ were used. On treatment with oxygen, the resonance disappeared. Analysis of the spectra yielded values of $g_{\parallel} = 1.942$, $g_{\perp} = 1.995$, and $B = 0.00125\ cm^{-1}$. Uncertainties in the g values were estimated to be on the order of ± 0.01.

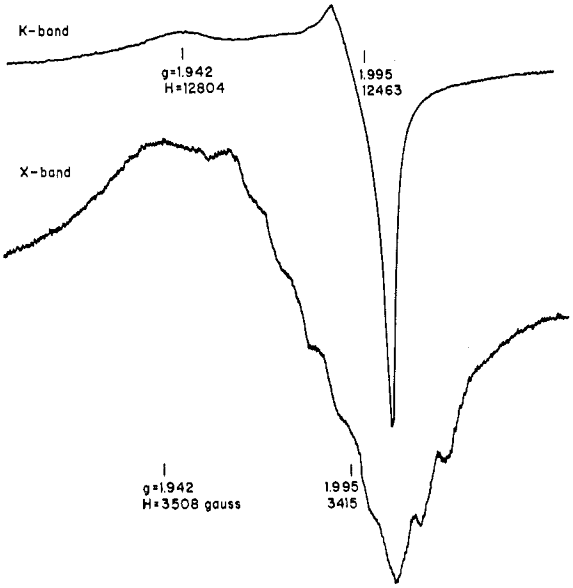

Figure 4.—X- and K-band esr spectra of Na_4CoPTS–NaCN complexes in DMSO at 77°K.

Visible spectra of the deoxygenated solutions of the Na_4CoPTS showed marked changes on addition of cyanide and subsequent further change on treatment with oxygen. In the presence of cyanide ion, the initial bands (663, 600, 332 mμ) were replaced by absorptions at 678, 610, 468, 430, and 325 mμ. On contact with oxygen, the low-energy bands increased in intensity, the band at 468 mμ disappeared, and a substantial decrease in the intensity at 430 mμ was observed. The final spectrum was the same as that reported by Day and coworkers[16] for cobalt(III) phthalocyanine complexes. The spectrum observed in the absence of oxygen was that expected for a mixture of Co(III) and Co(I) species.[14] Since both species are diamagnetic, such an interpretation leaves unexplained the observed esr spectrum of these solutions.

Discussion

DMSO, py, imid.—The effects of extraplanar ligands on the esr spectra of DMSO solutions of Na_4CoPTS in the absence of molecular oxygen are shown in Figures 1 and 2. Since the bonding of the Co to the four nitrogens in the phthalocyanine skeleton is expected to remain essentially invariant on coordination with extraplanar ligands, the origin of these spectral changes should, to a good approximation, be localized in the a_{1g} orbital.

The esr spin-Hamiltonian parameters obtained from analysis of the paramagnetic resonance spectra are summarized in Table I. Earlier attempts to correlate the spin-Hamiltonian parameters in low-spin cobalt(II) systems with the basicity and the charge density of the nitrogen donor atom of the extraplanar ligands have been hampered by the incomplete resolution of the perpendicular regions of the spectra. Thus it was concluded that, for example, in CoTPP complexes, these spectroscopic parameters are quite insensitive to the basicity or π-bonding ability of the ligand. A similar insensitivity to simple ligand basicity but a correlation with π-electron density was found for CoPc complexes with pyridine and quinolines.[7]

The ligands cyanide, imidazole, and pyridine were chosen for the present study because the N donors in these ligands exhibit opposite trends in basicity and in π-bonding ability. Imidazole, with a higher charge density on the coordinating nitrogen, is a much stronger base but a weaker π acceptor than pyridine. On the other hand, cyanide, the strongest base, is also a good π acceptor.

The results summarized in Table I show a small but regular decrease in A_{Co} as DMSO is replaced by one or two imidazoles or pyridines. Imidazole, the stronger base, produces the greater effect in both the 1:1 and 1:2 complexes. Much more pronounced, however, are the effects of these extraplanar ligands on B_{Co}. Here, again, the effects are much more marked in the 2:1 than in the 1:1 complexes. Since A_{Co} and B_{Co} are small, poor spectral resolution in the earlier studies may have led others to conclude that the esr parameters are insensitive to ligand basicity.

Oxygen Adducts.—Attempts to prepare the complexes L–NaCoPTS–O_2, where L = DMSO or py, were unsuccessful. With L = imidazole, however, such adducts may have been formed initially, but the reaction apparently proceeded further. Indeed, the oxygen-sensitive signal at $g = 1.984$ may have been a portion of the perpendicular region of the spectrum of the desired 1:1 O_2 adduct.

If the oxygen-insensitive resonances in the case of the imidazole complex were those of the simple adduct, spectra similar to those observed in other cobalt complexes[8–12] would have been expected. Furthermore, we should have noted differences in the shape of the very intense perpendicular region between the X- and K-band spectra.[15] Our failure to observe such differences and the apparent inconstancy of the ratio of the intensities of the signals at $g = 1.99$ and $g = 2.04$ led us to conclude that two species were present.

The spectrum at $g = 2.04$ ($A_{Co} = 16$ G) is very similar to that reported for the superoxo-bridged dimers of pentaamminecobalt, although the coupling constant is larger than expected.[17] In the pentaammine complex, values of $g = 2.025$ and $A_{Co} = 11.4$ G were previously reported. The incomplete, unsymmetrical resolution

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[17] E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959).

of the hyperfine components for our $g = 2.04$ signal (8–11 were generally resolved) is, however, reminiscent of the spectra reported by Ebsworth and Weil. We conclude then that the evidence favors the assignment of this resonance to a species of the form [imid·Na_4-CoPTS]–O_2–[Na_4CoPTS·imid].

The origin of the third signal is unknown. The data seem best described by the parameters $g_{\parallel} = 1.991$ and $g_{\perp} = 1.999$. Kwan and coworkers[9] have observed a signal at $g = 2.00$ on exposure of trichloroacetic acid solutions of CoPc to oxygen, which they attribute to the first step in the destructive oxidation of the phthalocyanine. Both oxidation to Co(III) and oxidation of the ring can be followed by changes in the visible spectra, however. In our studies no such changes in the visible spectrum were observed, suggesting that the radicals we observed did not involve the phthalocyanine π system.

NaCN.—Coordination of cyanide, in the absence of oxygen, to Na_4CoPTS produced a series of very surprising changes. Busch and coworkers[18] had earlier reported that an oxidation process occurs under conditions similar to ours, which is then apparently accompanied by destruction of the cyanide anion. In aqueous solution the product obtained was the hydroxocobalt(III) complex. Our visible spectral and esr data may lend some insight into the mechanism of this reaction.

Our esr data on the pyridine and imidazole complexes indicated an increasing effect of these extraplanar ligands on the electronic structure of the cobalt with increasing ligand basicity. With the most basic of the ligands used, cyanide, the typical Co(II) spectrum was replaced by that depicted in Figure 4. Visible spectra showed the presence of a Co(I) and a Co(III) species, both diamagnetic, in solution. On exposure to oxygen, only the Co(III) complex was retained. No visible spectral evidence was obtained for ligand degradation or for replacement of the phthalocyanine ligand by cyanide.

Our visible spectral results indicate that the Co(II) complex is unstable in the presence of cyanide, disproportionating to Co(I) and Co(III) species. The esr data suggest a possible mechanism for this disproportionation reaction. From the g and A values for the radical species (Figure 4), it is unlikely that the lone electron is localized in a cobalt d orbital. We therefore conclude that the initial step in the disproportionation is an "intramolecular" oxidation–reduction reaction of Co(II) to yield $Na_4Co(III)PTS^- \cdot x$NaCN, with the lone electron localized principally in the π system of the phthalocyanine ring. This conclusion is supported by the observation of eight hyperfine lines in the perpendicular region of the spectrum, tentatively attributed to the cobalt, and by our failure to observe a change in the spectrum when isotopically labeled cyanide (^{13}C and ^{15}N, $I = {}^1/_2$) was used.

Summary

The effects of the extraplanar ligands py, imid, and cyanide on the esr spin-Hamiltonian parameters of cobalt phthalocyanine complexes have been examined. These effects, which parallel basicity, were significantly greater in the 2:1 than in the 1:1 complexes and were more evident in the heretofore unresolved perpendicular regions ($g_{\perp}$, B_{Co}) than in the parallel regions of the spectra.

Weber and Busch[18] had observed a substantial change in the effective magnetic moment of these complexes as L is varied from pyridine to imidazole to cyanide, with the cyanide complex exhibiting essentially a free-electron value. Our results indicate that, in the case of cyanide, the complex no longer contains divalent cobalt, and we have interpreted the esr spectrum of this system in terms of a Co(III) complex of the phthalocyanine anion with the unpaired electron localized primarily on the phthalocyanine ring.

Attempts to prepare the 1:1 oxygen adducts L–Na_4CoPTS–O_2 were unsuccessful. Where probable complex formation was suggested in the case of imidazole, further irreversible reaction was indicated. The esr spectra suggested three paramagnetic intermediates in this oxidation process, among them probably the superoxo-bridged dimer.

These results, when compared with those previously reported for cobaloxime and CoTPP complexes, indicate the subtle but important differences in the chemistry which can exist within a group of such similar B_{12} models. For example, bis-imidazole complexes have not been observed for either of these alternative model systems, but they do exist for the phthalocyanines. In addition, the data presented here provide some indication of the nature and the magnitude of the changes which can be expected in the esr spectra of these B_{12} model compounds, their base adducts, and, possibly, other low-spin Co(II) complexes.

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