New Adducts of Phthalocyaninatocobalt(II) with Pyridine and 4-Methylpyridine and their Vibrational, Magnetic, and Electronic Properties. Part I. Reactivity towards Oxygen

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Different reaction temperatures have allowed the isolation of 1 : 1 and 1 : 2 adducts of phthalocyaninatocobalt(II) with pyridine and 4-methylpyridine. Thermal, vibrational, and magnetic-susceptibility analyses have provided useful information about the structural properties of these complexes; e.s.r. and electronic spectra have permitted a detailed investigation of the ligand-field levels of the cobalt atom. All the adducts react with oxygen and form, at low temperatures, well characterized Co : O_2 1 : 1 adducts.

THE large number of papers on the properties and chemical reactivity of phthalocyanine complexes published in the last few years [1-4] emphasizes the continual interest shown in these compounds. Their structural similarity with the heme proteins suggests that transition-metal phthalocyanines can be used as model compounds for natural products; [2,5] in addition, the catalytic activity [6,7] shown in oxygen reduction or in oxidative dehydrogenation suggests that investigation of the catalysis mechanism can be further extended. The ability of [Co(pc)] [pc = phthalocyaninato(2−)] to co-ordinate base molecules is well known and e.s.r. investigations on [Co(pc)] in basic solutions have been reported; [8] however, well characterized solid compounds have never been described. In the present paper, syntheses of 1 : 1 and 1 : 2 adducts of [Co(pc)] with pyridine (py) and 4-methylpyridine (4-Mepy) are described together with their vibrational, magnetic, and electronic properties; the relation between planar and five- and six-co-ordination in such complexes has also been investigated.

EXPERIMENTAL

Synthesis of Complexes.—*Phthalocyaninatocobalt*(II), [Co(pc)]. This complex was synthesized as previously described,[3,9] and both polymorphs, α and β, were obtained.

Phthalocyaninato(pyridine)cobalt(II), [Co(pc)(py)]. A suspension of [Co(pc)], in either the α or β form, was heated under reflux in purified pyridine until the solid was completely dissolved. After cooling to 100 °C, a blue amorphous *powder* similar to [Co(pc)] was obtained. The filtered solid was dried *in vacuo* (2 mmHg) to constant weight. Elemental and thermal analysis conclusively proved that a new complex, containing one py for each [Co(pc)] unit, had been obtained (see Table 1). The complex has a very low solubility and only dissolves in boiling py. Hence a better preparative method is to extract with py the complex [Co(pc)] in a Soxhlet apparatus. This process assures complete dissolution with the minimum amount of solvent and easier precipitation of the required product.

TABLE 1

Analytical data (%) for the cobalt complexes

Complex	Found Co	Found Base *	Calc. Co	Calc. Base
[Co(pc)]	10·25		10·3	
[Co(pc)(py)]	8·70	12·0	8·90	12·0
[Co(pc)(py)$_2$]	7·90	21·3	8·10	21·0
[Co(pc)(4-Mepy)]	8·65	14·2	8·90	14·0
[Co(pc)(4-Mepy)$_2$]	7·70	23·0	7·80	24·0

Base = Pyridine or 4-methylpyridine.

* Obtained by thermal analysis.

Phthalocyaninatodi(pyridine)cobalt(II), [Co(pc)(py)$_2$]. On allowing the above refluxed or extracted solution to stand at room temperature for at least 12 h, a new solid very similar to [Co(pc)(py)] (except for the more crystalline appearance) was obtained. Its elemental and thermal analysis corresponded to a 1 : 2 adduct (see Table 1). It is readily soluble in CH_2Cl_2, toluene, acetone, and other non-co-ordinating solvents; however, after a few seconds, it loses both py molecules and decomposes to β-[Co(pc)]. The complex [Co(pc)(py)$_2$] may also be obtained from a stirred suspension of [Co(pc)] in py at room temperature in *ca.* 12 h, the product was separated by filtration and dried *in vacuo*. The preparation of [Co(pc)(py)$_2$] from [Co(pc)(py)] is also possible; [Co(pc)(py)] was suspended in py at room temperature for *ca.* 1 d, the conversion being a slow process. The complex [Co(pc)(py)$_2$] can be reconverted to [Co(pc)(py)] by heating a suspension of the former under reflux in py, and rapidly filtering the hot solution.

(*4-Methylpyridine*)- *and di*(*4-methylpyridine*)-*phthalocyaninatocobalt*(II), [Co(pc)(4-Mepy)] *and* [Co(pc)(4-Mepy)$_2$].

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[1] J. S. Griffith, *Discuss. Faraday Soc.*, 1958, **26**, 81.

[2] J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discuss. Faraday Soc.*, 1958, **26**, 72.

[3] J. M. Assour and W. K. Kahn, *J. Amer. Chem. Soc.*, 1965, **87**, 207.

[4] L. M. Engelhardt and M. Green, *J.C.S. Dalton*, 1972, 724.

[5] D. J. E. Ingram, ' Biological and Biochemical Applications of Electron Spin Resonance,' Adam Hilger, London, 1969.

[6] M. Savy, P. Andro, C. Bernard, and G. Manger, *Electrochim. Acta*, 1973, **18**, 191.

[7] J. Manassen and A. Bar-Ilan, *J. Catalysis*, 1970, **17**, 86.

[8] J. M. Assour, *J. Amer. Chem. Soc.*, 1965, **87**, 4701.

[9] P. A. Barrett, C. E. Dent, and R. P. Linstead, *J. Chem. Soc.*, 1936, 1719.

The syntheses of these adducts were not very different from those of the py adducts, except that there was less difference between the solubility of the 1 : 1 and the 1 : 2 adducts with 4-methylpyridine. Hence it was more difficult to separate the pure products. In order to obtain [Co(pc)(4-Mepy)], the best experimental conditions were to extract [Co(pc)] in a Soxhlet apparatus with a small amount of 4-Mepy and to rapidly filter the hot solution before [Co(pc)(4-Mepy)$_2$] could coprecipitate. The complex [Co(pc)(4-Mepy)$_2$] was precipitated from the extracted solution at room temperature and appeared as a microcrystalline blue powder, unlike the amorphous 1 : 1 adducts. Both complexes were dried under vacuum to constant weight. (For the elemental analyses see Table 1.) The interconversion of [Co(pc)(4-Mepy)] and [Co(pc)(4-Mepy)$_2$] is also possible, but this process is faster than with the analogous py adducts, while the reverse process requires a longer reflux.

Spectroscopic, Magnetic, and Thermal Measurements.—Thermal analyses were carried out on a Dupont 900 apparatus equipped with a thermogravimetric analyser Dupont 950 at a heating rate of 1 °C min^{-1} under a stream of nitrogen at 40 cm^3 min^{-1}. Cobalt analyses were made with a Varian Techtron atomic-absorption spetrophotometer. Magnetic susceptibilities were obtained by the Gouy method. E.s.r. spectra were recorded on a Varian 4502-11 spectrometer at a field modulation of 100 kHz. The resonance frequencies were derived by standardization with diphenylpicrylhydrazyl. Reflectance electronic spectra were recorded on a Beckman DK-2A spectrophotometer, and i.r. spectra on a Perkin-Elmer 621 spectrophotometer.

RESULTS

Thermal Behaviour of [Co(pc)] *Adducts with Bases.*—The thermograms of the [Co(pc)] adducts (Figure 1) outline the specific preparative methods of these complexes; while for similar cobalt complexes adducts of different stoicheiometry were obtained by means of different base–complex ratios,[10] in our case the different reaction temperature decided the product. In the case of the py adducts, when the synthesis was conducted at 115 °C (boiling py), only one base molecule bound to [Co(pc)]; however, when the solution was allowed to cool the 1 : 2 adduct was stabilized and a short period of cooling produced a mixture of 1 : 1 and 1 : 2 adducts. In the case of 4-Mepy, the smaller difference between the temperatures of base dissociation gave rise to the great difficulty in separating the 1 : 1 and 1 : 2 adducts.

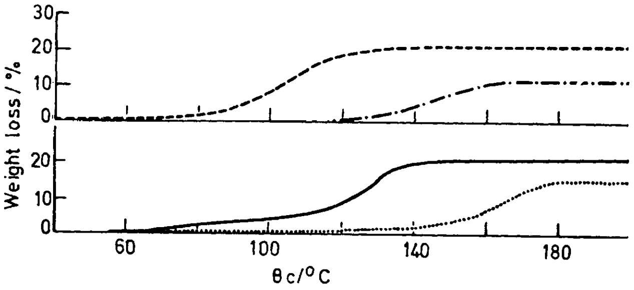

FIGURE 1 Thermograms of [Co(pc)] adducts: (— · — · —), [Co(pc)(py)]; (— — —), [Co(pc)(py)$_2$]; (· · · ·), [Co(pc)(4-Mepy)] and (——), [Co(pc)(4-Mepy)$_2$]

From the thermograms it is evident that the chemical bonds between the base and the Co^{II} ion are very different from one adduct to another. All the 1 : 2 adducts contain two equivalent bonds, which break easily and simultaneously. There was no evidence of formation of the 1 : 1 adduct by thermal dissociation. The bonding strength is greater for the 1 : 1 adducts, as shown by the fact that base dissociation was slower in these complexes. It is worth noting that thermal dissociation of the base adducts gives different complexes. On heating [Co(pc)(py)], α-[Co(pc)] was obtained, while from [Co(pc)(py)$_2$] the complex β-[Co(pc)] was obtained. It is believed that this is a very important reaction for (*a*) it gives a new preparative method for obtaining highly pure α- and β-[Co(pc)], and (*b*) it suggests a structural similarity between α-[Co(pc)] and [Co(pc)(py)] and β-[Co(pc)] and [Co(pc)(py)$_2$]. By thermal dissociation, both adducts of 4-Mepy gave a mixture of α- and β-[Co(pc)].

Vibrational Properties.—A comparison of the i.r. spectra of α- and β-[Co(pc)] with those of its base adducts is shown in Table 2. The range of vibrational frequencies considered was from 850 to 600 cm^{-1}, because in this range the intermolecular linkages, the differences in latticing,[11,12] and the base-molecule vibration [13] are detectable. As regards the skeletal vibrations of the phthalocyanine, the spectra of [Co(pc)(py)$_2$], α-[Co(pc)], and β-[Co(pc)] showed an identical number of bands, while the number increased in [Co(pc)(py)]. It is believed, therefore, that the co-ordination of one py molecule reduces the vibrational degeneracy. It was also observed that the planar-ligand frequencies of [Co(pc)(py)$_2$] were more similar to those of β-[Co(pc)] than α-[Co(pc)]; likewise [Co(pc)(py)] seems to be more similar to α-[Co(pc)]. If the differences found in the spectra of α- and β-[Co(pc)] mean that the two polymorphs have different intermolecular interactions,[11,12] it can be supposed that, as regards the intermolecular interactions, [Co(pc)(py)] is similar to α-[Co(pc)] and [Co(pc)(py)$_2$] to β-[Co(pc)]. The spectra of both 4-Mepy adducts were quite similar, without any reduction in vibrational degeneracy of the parent complex, and their skeletal vibrations assumed an intermediate position between α- and β-[Co(pc)]. All the skeletal-frequency similarities here observed are in agreement with the molecular similarities derived from the thermal analyses.

TABLE 2

I.r. spectra from 850 to 600 cm^{-1} in Nujol mulls

Complex	Bands/cm^{-1}
β-[Co(pc)]	780m, 755s, 733vs
α-[Co(pc)]	771m, 755s, 722vs
[Co(pc)(py)]	773m, 763m, 753s, 725vs, 718s, 700m,* 614w *
[Co(pc)(py)$_2$]	778m, 753s, 728vs, 698m,* 609w *
[Co(pc)(4-Mepy)]	803m,* 776m, 754s, 733vs
[Co(pc)(4-Mepy)$_2$]	803m,* 776m, 753s, 733vs

w = Weak, m = medium, s = strong, and vs = very strong.

* Due to co-ordinated base.

Magnetic Properties.—The results of the magnetic-susceptibility measurements are reported in Table 3 [3,14,15] and it is observed that, on going from [Co(pc)] to [Co(pc)(py)$_2$], the values approach that of an octahedral low-spin Co^{II} complex.[16] Although no resonance lines were obtained from undiluted α- and β-[Co(pc)], all the base adducts gave

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[10] F. A. Walker, *J. Amer. Chem. Soc.*, 1970, **92**, 4235.

[11] D. N. Kendall, *Analyt. Chem.*, 1953, **25**, 382.

[12] A. A. Ebert, jun., and H. B. Gottlieb, *J. Amer. Chem. Soc.*, 1952, **74**, 2806.

[13] N. S. Gill, R. H. Nutall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.

[14] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1959, 338.

[15] R. Havemann, W. Haberditzl, and K. H. Mader, *Z. phys. Chem.* (*Leipzig*), 1961, **218**, 71.

[16] R. C. Stoufer, D. N. Smith, E. A. Clevanger. and T. E. Norris, *Inorg. Chem.*, 1966, **5**, 1167.

TABLE 3

Magnetic moments and e.s.r. data on polycrystalline samples

Complex	$\mu_{eff.}$ [a]/B.M.	$g_\perp$ [b]	$g_\parallel$ [b]
β-[Co(pc)]	2·72 [c]		
α-[Co(pc)]	2·38 [c]		
[Co(pc)(4-Mepy)]	2·42	2·27	2·11
[Co(pc)(4-Mepy)$_2$]	2·12	2·21	2·02
[Co(pc)(py)]	2·03	2·28	2·13
[Co(pc)(py)$_2$]	1·90	2·20	2·01
[Co(salen)] ' monomeric '	2·72 [d]		
[Co(salen)] ' inactive '	2·17 [d]		
[Co(salen)(py)]	2·22 [d]		

[a] At room temperature; 1 B.M. 9·27 × 10^{-21} erg G^{-1}. [b] At 113 K. [c] Refs. 3, 14, and 15. [d] Ref. 24.

e.s.r. spectra as polycrystalline samples (Figure 2). The complexes showed axial magnetic symmetry, with two principal g values (Table 3). From the line intensities it is not difficult to assign the low-field resonances to $g_\perp$ and those at higher field to $g_\parallel$. Resolved hyperfine coupling was hindered in the polycrystalline sample, but it was observed that co-ordination of basic units in axial positions shifts the $g_\perp$ value of [Co(pc)] towards higher fields, the greater the strength of the axial ligand. For two base molecules co-ordinated the shift was larger than for one molecule. The values of the g tensors of the adducts could not be accurately measured; however, it is clear that there is no great difference between the magnetic-tensor values of py and 4-Mepy.

TABLE 4

E.s.r. parameters

Complex	$g_\perp$	$g_\parallel$	$10^4A_\perp$ cm^{-1}	$10^4A_\parallel$ cm^{-1}	10^4A_N cm^{-1}	b_2	b_3	Energy (10^3 cm^{-1}) of the transition $z^2 \leftarrow (xz, yz)$
β-[Co(pc)] [a]	2·94	1·89	280	150		(−0·1531)	(0·9763)	(2·26)
α-[Co(pc)] [b]	2·60	1·99	64	110		(−0·0921)	(0·9915)	(3·70)
[Co(pc)(4-Mepy)] [c]	2·32	2·005	15	98	16	(−0·0475)	(0·9977)	(7·30)
[Co(pc)(4-Mepy)$_2$] [d]	2·25	2·015	12	77	14	(−0·0368)	(0·9986)	(9·40)

Calculated values are given in parentheses.

[a] Ref. 3. [b] Powder of α-[Zn(pc)] diluted by α-[Co(pc)]. [c] 4-Mepy Solution. [d] 4-Mepy–CH_2Cl_2 (70% base) solution.

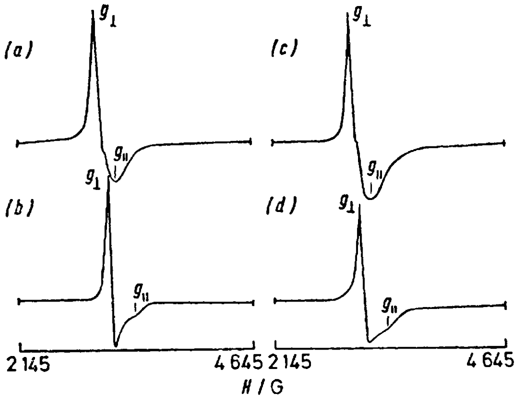

FIGURE 2 E.s.r. spectra of the polycrystalline complexes: (a), [Co(pc)(py)]; (b), [Co(pc)(py)$_2$]; (c) [Co(pc)(4-Mepy)]; and (d), [Co(pc)(4-Mepy)$_2$]

E.s.r. spectra of [Co(pc)(py)$_2$] and [Co(pc)(4-Mepy)$_2$] were also recorded in frozen solutions of CH_2Cl_2 with various amounts of base, under an atmosphere of nitrogen. With a large excess of base, clearly detectable [Co(pc)(py)$_2$] and [Co(pc)(4-Mepy)$_2$] signals were observed (Figure 3, Table 4), but the values of the magnetic parameters of [Co(pc)(4-Mepy)$_2$] are not in agreement with those recorded by Assour.[8] At low field, besides the resonance lines due to the 1 : 2 adducts, an unresolved signal which cannot be attributed to the [Co(pc)(base)$_2$] complexes was clearly observable. With low base concentration, the lines due to [Co(pc)(base)$_2$] decreased in intensity, while the unresolved signal remained unchanged. It is believed that this signal is attributable to an inhomogeneous species, most probably a polycrystalline [Co(pc)(base)] adduct. This conclusion was confirmed by the fact that the unresolved signal and the signal found in the spectra of polycrystalline [Co(pc)(py)] and [Co(pc)(4-Mepy)] were identical.

It is proposed that in mixtures of CH_2Cl_2 and base solvents there are equilibrium reactions [equation (1)] whose position

$$[Co(pc)(base)_2] \rightleftharpoons base + [Co(pc)(base)] \rightleftharpoons [Co(pc)(base)](s) \quad (1)$$

is regulated by the amount of base. As the 1 : 1 adducts are more insoluble than the 1 : 2 adducts, a resolved spectrum of [Co(pc)(base)] was not obtainable at 113 K. Nevertheless in the case of [Co(pc)(4-Mepy)] it was possible to record the e.s.r. spectrum under very specific conditions in which [Co(pc)] was dissolved in 4-Mepy and rapidly frozen to 113 K (Figure 4). An analogous spectrum has been erroneously attributed by Assour [8] to [Co(pc)(4-Mepy)$_2$] and this

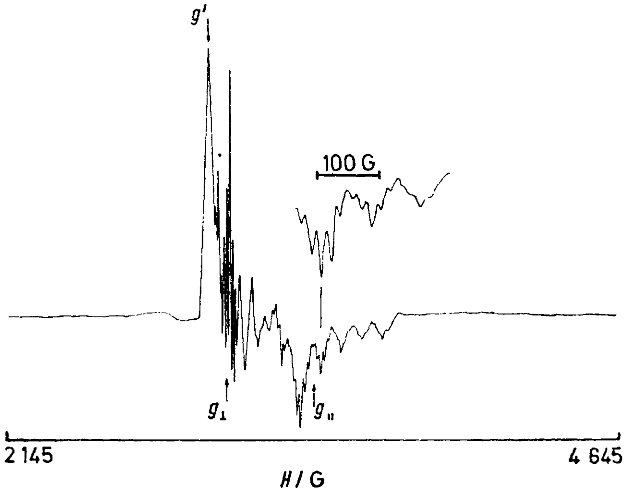

FIGURE 3 E.s.r. spectrum of [Co(pc)(4-Mepy)$_2$] in frozen 4-Mepy–CH_2Cl_2 (70%) solution; g' is attributed to the presence of polycrystalline [Co(pc)(4-Mepy)]

explains the differences between our magnetic parameter values and those of Assour.

The rapid freezing of a [Co(pc)] solution in py was attempted, but probably the concentration of [Co(pc)(py)] was too small to be detectable; a large amount of solid polycrystalline [Co(pc)] was observed in the presence of a little dissolved [Co(pc)(py)] and [Co(pc)(py)$_2$] and the overlap of the lines due to the dissolved species gave rise to a very complicated spectrum.

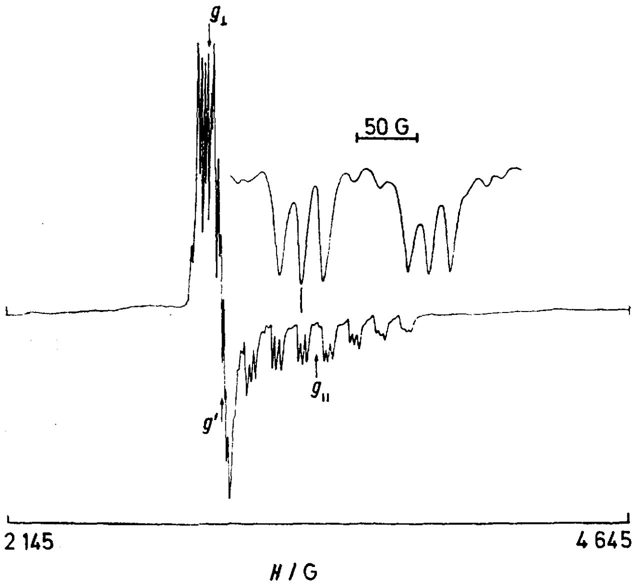

FIGURE 4 E.s.r. spectrum of [Co(pc)(4-Mepy)] in frozen 4-Mepy solution; g' is attributed to the presence of some [Co(pc)(4-Mepy)$_2$]

Calculations on the E.S.R. Results and Optical Properties.— In the light of g values previously reported, it is possible to make some extensive conclusions on the electronic perturbations which relate to [Co(pc)] from the addition of ligands at the fifth and sixth co-ordination positions. The main effect of axial-base co-ordination on the e.s.r. parameters of [Co(pc)] was to decrease the values of $g_\perp$ and increase those of $g_\parallel$ (see for example the trend in values for the 4-Mepy adducts in Table 4). In β-[Co(pc)], which has a known molecular structure,[17,18] it was observed that $g_\perp$ shifts from 2·94 to 2·32 after co-ordination of one 4-Mepy molecule and attains the minimum value of 2·25 after co-ordination of two molecules. The related values of $g_\parallel$ are respectively 1·89, 2·005, and 2·015. In this series of phthalocyanine derivatives, on the basis of its e.s.r. parameters, α-[Co(pc)] can be placed between the β form and the base adducts as regards structural properties. Therefore it is certain that the differences between α- and β-[Co(pc)] are due to an axial-bond interaction experienced by cobalt(II) in α-[Co(pc)]. The same trend was observed in a series of *NN'*-ethylenebis(salicylideneiminato)cobalt(II), [Co(salen)], adducts [19] where it was found that, on going from monomeric to dimeric [Co(salen)] and to its adduct with py, the $g_\perp$ values shift from 3·2 to 2·6 and 2·41 and the $g_\parallel$ values from 1·91 to 2·002 and 2·013. Monomeric [Co(salen)] can be compared to β-[Co(pc)] and dimeric [Co(salen)] to α-[Co(pc)].

To support our results a theoretical calculation of g- and A-tensor values was made using a second-order approximation. This method, as described in a previous paper,[20] led to a satisfactory reproduction of the experimental values and to a good evaluation of the cobalt ground state. The unpaired electron was found, as expected, in the d_{z^2} orbital, but there is some contribution also from the d_{xz} and d_{yz} orbitals. The results of the calculation are shown in Table 4 where b_1, b_2, and b_3 are related respectively to the weights of the d_{xz}, d_{yz}, and d_{z^2} orbitals in the ground state of the complexes ($b_1 = b_2$ for symmetry). By considering the b_i values, it was observed that the contribution of the d_{z^2} orbitals to the ground state increases from β-[Co(pc)] to α-[Co(pc)] to the base adducts. However the contributions of d_{xz} and d_{yz} decrease in the same order and this could mean that axial co-ordination is related to the higher percentage of the unpaired electron along the z axis. The second-order approximation is most useful in explaining the experimental magnetic data and, from expressions (2) and (3), it can be

$$g = 2b_3^2 - 4b_1^2 + 4Kb_1^2 \quad (2)$$

$$g_\perp = 2b_3^2 - 4K3^{\frac{1}{2}}b_1b_3 \quad (3)$$

calculated that, assuming $K = 1$, on decreasing the b_1 contributions b_3 and $g_\parallel$ must increase while $g_\perp$ decreases. This is in good agreement with the calculation of Engelhardt *et al.*[4] Therefore it is expected that $g_\parallel$ increases when the axial interaction becomes stronger. Applying a first-order approximation ($b_3 = 1$), no displacement of $g_\parallel$ from the g value of the free electron would be expected.[21]

The results of the e.s.r. measurements were confirmed by optical-spectroscopic investigations, mainly in the near-i.r. region. Figure 5 shows reflectance electronic spectra of α- and β-[Co(pc)] and of all the base adducts. In the near-i.r. region we observed: (*i*) an absorption at 5 200 cm^{-1} in the spectrum of β-[Co(pc)]; and (*ii*) an absorption at 4 400 cm^{-1} with shoulders at 8 500 and 9 600 cm^{-1} in the spectrum of α-[Co(pc)] and a shoulder at 10 400 cm^{-1} in all the spectra of the [Co(pc)] adducts with base molecules. The bands at 5 200 and 4 400 cm^{-1} can be assigned to *d–d* transitions, on the basis of their intensity. For the other bands, which

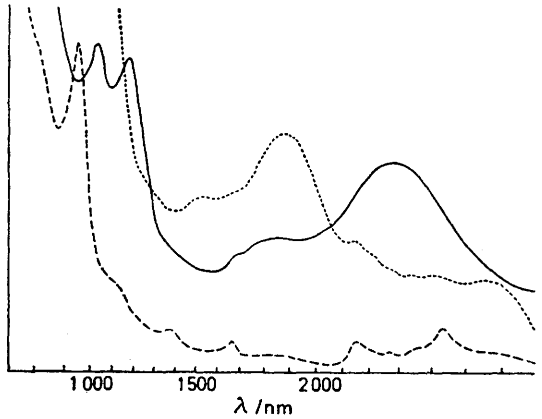

FIGURE 5 Reflectance electronic spectra: (——), α-[Co(pc)]; (· · · ·), β-[Co(pc)]; and (– – – –), [Co(pc)(py)$_2$]

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[17] J. M. Robertson, 'Organic Crystals and Molecules,' Cornell University Press, New York 1953.

[18] F. H. Moser and A. L. Thomas, 'Phthalocyanine Compounds,' Reinhold Publishing Corp., New York, 1963.

[19] C. Busetto, F. Cariati, P. Fantucci, D. Galizzioli, and F. Morazzoni, *J.C.S. Dalton*, 1973, 1712.

[20] C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J.C.S. Dalton*, 1973, 754.

[21] A. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, 1964, **86**, 4580.

appear as shoulders on the very strong absorption, an unambiguous assignment is less readily obtainable. By comparing spectra of the free ligand and [Zn(pc)] with those of α- and β-[Co(pc)] and its base adducts, it is proposed that the shoulders at 8 500, 9 600, and 10 400 cm^{-1}, observed respectively in α-[Co(pc)] and in the base adducts, can be ascribed to *d–d* transitions, at least as regards the main component of the state involved in the electron transfer. All the other bands of lower intensity found in the cobalt complexes are due to ligand absorptions.

The calculation method which reproduces the experimental values of the magnetic tensors can also be used to calculate the energies of the *d–d* transitions between the doublet states spin–orbit interacting with the ground state $(xz,yz)^4(x^2 - y^2)^2(z^2)$. Hence, the energy of the one-electron transition from $(xz,yz)^4(x^2 - y^2)^2(z^2)$ to $(xz,yz)^3(x^2 - y^2)^2(z^2)^2$ can be calculated, while the transition from the ground state to $(xz,yz)^4(x^2 - y^2)(z^2)^2$ cannot be calculated because of the lack of spin–orbit mixing between this configuration and that of the ground state. The absorption at 4 400 cm^{-1} found in α-[Co(pc)] is mainly related to the $g_\perp$ value and can be associated with the one-electron transition $(xz,yz)^4(x^2 - y^2)^2(z^2) \rightarrow (xz,yz)^3(x^2 - y^2)^2(z^2)^2$ (see Table 4) where the transition is indicated $(xz,yz \rightarrow z^2)$. For β-[Co(pc)] the same transition was expected to shift to 2 000 cm^{-1} due to the increase in the $g_\perp$ value and in fact no absorption was found in the region between 4 500 and 3 400 cm^{-1}. In the adducts of [Co(pc)] with base molecules, the $xz,yz \rightarrow z^2$ transition must shift to higher frequencies (see Table 4), but any assignment is very difficult because of the presence of strong bands in this region; on the other hand the assignment of the band found in the 1 : 1 and 1 : 2 adducts at 10 400 cm^{-1} to a $xz,yz \rightarrow z^2$ transition is improbable because, on passing from the 1 : 1 to the 1 : 2 adducts, its frequency must change as the $g_\perp$ values change.

None of the calculated *d–d* transitions reproduced the band at 5 200 cm^{-1} found in the spectrum of β-[Co(pc)]. Therefore, since this is an electronic *d–d* absorption, it can be tentatively attributed to the $x^2 - y^2 \rightarrow z^2$ transition involving doublet states which do not interact by spin–orbit coupling. The same transition was shifted very probably to 8 500 and 9 600 cm^{-1} in α-[Co(pc)] and perhaps to 10 400 cm^{-1} in the base adducts. It should be noted that these assignments are very similar to the trend in [Co(salen)] and related complexes.[19,20] On passing from planar- to axial-co-ordinated complexes, the greater difference is in the weight of d_{z^2} orbital in the ground state. The trend in d_{z^2} orbital contribution is therefore $[\text{Co(pc)(base)}_2]$ (base = py or 4-Mepy) > [Co(pc)(base)] > [α-Co(pc)] > β-[Co(pc)].

On the basis of the electronic and magnetic measurements, the same reasons for the activation towards oxygen suggested by us in previous work [19,20,22] are available also for the [Co(pc)] adducts, and could be favourable to their reaction with O_2. A solution containing $[\text{Co(pc)(base)}_2]$, dissolved in CH_2Cl_2 and various amounts of base, was exposed to the air. It was observed that, on decreasing the base concentration, the resonance lines due to $[\text{Co(pc)(base)}_2]$ decreased in intensity while a new signal due to a 1 : 1 Co : O_2 adduct [23] increased. The best conditions for obtaining a large amount of oxygen adduct seem to be in a solution of $[\text{Co(pc)(base)}_2]$ in CH_2Cl_2, but, in this case, $[\text{Co(pc)(base)}_2]$ loses both the base molecules giving insoluble β-[Co(pc)]. The oxygen absorption of $[\text{Co(pc)(base)}_2]$ is a quantitative process in $PO(NMe_2)_3$ where the dissociation of $[\text{Co(pc)(base)}_2]$ to [Co(pc)(base)] is favoured. It is believed that the greater the release of one base molecule, the greater is the yield of the oxygenation product and it can be concluded that the displacement of one molecule of base from $[\text{Co(pc)(base)}_2]$ is the first condition for reactivity towards oxygen.

DISCUSSION

The aim of this discussion is to clarify, on the basis of the thermal, spectroscopic, and magnetic results, the structural relation between α- and β-[Co(pc)] and to postulate the structure of the [Co(pc)] adducts with py and 4-Mepy.

The first hypothesis concerning the differences between the two polymorphs of [Co(pc)] was suggested by Assour *et al.*[3] The results of their investigations led Assour *et al.* to conclude that in β-[Co(pc)] the cobalt(II) experiences an axial interaction derived from neighbouring molecules which is stronger than that in α-[Co(pc)]. Some years later Engelhardt and Green [4] carried out an extensive calculation on [Co(pc)] and analogous derivatives and concluded that the more axial interaction with cobalt(II) the more $g_\perp$ decreases and $g_\parallel$ increases, and in the case of α-[Co(pc)] the axial interaction involving Co^{II} seemed to these authors stronger than for β-[Co(pc)].

Structural differences between α- and β-[Co(pc)], which until now were unresolved because of the lack of an *X*-ray crystal analysis for α-[Co(pc)], have now been reconsidered and the calculations of Engelhard and Green have been confirmed. In the present magnetic-susceptibility measurements it was observed that on passing from β-[Co(pc)] to α-[Co(pc)] to the [Co(pc)] base adducts the μ values decreased, with the value of α-[Co(pc)] much closer to those of the base adducts than to that of β-[Co(pc)]. A similar trend in magnetic moments was found in the series [Co(salen)] (' active ' form), [Co(salen)] (' inactive ' form), and [Co(salen)(py)] [24] (Table 3) where *X*-ray analyses confirmed that the axial interaction involving Co^{II} increases from the 'active' [Co(salen)] to [Co(salen)(py)].[25,26]

The previous discussion of the assignment of *g*-tensor changes confirms that, rather than considering α-[Co(pc)] as only a polymorph of β-[Co(pc)], it is better to consider it as a complex with a different co-ordination number for the cobalt ion. It is possible that the cobalt in α-[Co(pc)] gains a different co-ordination number by interaction with another molecule of [Co(pc)]. In this paper it is reported that α-[Co(pc)] and β-[Co(pc)] can also be obtained by heating respectively [Co(pc)(py)] and $[\text{Co(pc)(py)}_2]$ and, further, the products of thermal dissociation are expected from the vibrational analogies between [Co(pc)(py)] and α-[Co(pc)] and $[\text{Co(pc)(py)}_2]$ and β-[Co(pc)]. On this basis it is suggested that, as in

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[22] C. Busetto, F. Cariati, P. Fantucci, D. Galizzioli, F. Morazzoni, and V. Valenti, *Gazzetta*, 1972, **102**, 1040.

[23] C. Busetto, F. Cariati, D. Galizzioli, and F. Morazzoni, *Gazzetta*, 1974, **104**, 161.

[24] A. Earnshaw, P. C. Hawlett, E. A. King, and L. F. Larkworthy, *J. Chem. Soc.* (*A*), 1968, 241.

[25] (*a*) S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, 1969, **B25**, 1671; (*b*) M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1970, 2411.

[26] W. P. Schaefer and R. E. Marsh, *Acta Cryst.*, 1969, **B25**, 1675.

α-[Co(pc)], in [Co(pc)(py)] there is some intermolecular interaction involving the sixth co-ordination site, axially opposite to the py molecule. The complex [Co(pc)(py)$_2$] must be monomeric with no intermolecular interactions. In fact its thermal decomposition gives β-[Co(pc)] for which *X*-ray analysis [17,18] has not found an intermolecular distance that supports any bond interaction. That the sixth position around cobalt in [Co(pc)(py)] is not free has also been confirmed by the slow addition of another py molecule to [Co(pc)(py)]. If the co-ordination site was free and available for the bonding of the second base molecule, there would be no reason for the long time required for conversion of [Co(pc)(py)] to [Co(pc)(py)$_2$]. It was quite impossible until now to explain how [Co(pc)(4-Mepy)$_2$] could be similar to [Co(pc)(4-Mepy)], either as regards vibrational properties or the products of thermal dissociation, because it seemed impossible to claim an intermolecular interaction involving the six-co-ordinate cobalt ion in [Co(pc)(4-Mepy)$_2$].

Some conclusions, both as regards the chemistry of the planar cobalt complexes and the related bioinorganic and catalytic problems, can now be made. The [Co(pc)] molecule seems to have a great affinity for co-ordination of two base molecules as with all porphyrin or porphyrin-like complexes. Even when there is only one base molecule bonded to [Co(pc)], six-co-ordination is attempted through intermolecular interactions {as in the case of [Co(pc)(py)]}. Very probably the addition of only one base molecule could cause, as in the case of [Co(salen)(py)],[25b] folding of the planar ligand and displacement of the cobalt out of the molecular plane.[27] The rigidity of the phthalocyanine ring hinders these effects and therefore the phthalocyanine complexes require an axial interaction symmetrical to the equatorial-ligand plane.[28]

The general tendency of the base adducts of [Co(pc)] to assume six-co-ordination suggests that the reaction with oxygen must be preceded by a molecular rearrangement to free the sixth position on the metal atom. The inactivity of [Co(pc)(py)$_2$] shows that the oxygen molecule cannot substitute a basic molecule, very probably because it has an acid role in the adduct, and that the freeing of a co-ordination site is a process indispensable for oxygen absorption. The behaviour of the [Co(pc)] adducts in the reaction with oxygen is more similar to that of the heme proteins than the behaviour of the [Co(salen)(py)] complex.[29] In the hemoglobin molecule there are two histidine molecules at the metal ion, the 'distal' which is displaced when O_2 approaches and the 'proximal' which remains bonded to the metal when O_2 has been absorbed. It has been suggested [30] that the catalysis mechanism involves an intermediate adduct between the metal complex and the O_2^- anion; by characterizing the [Co(pc)(base)(O_2)] adduct this has now been proved, although at room temperature the interaction between O_2 and [Co(pc)] is not stable enough for [Co(pc)(base)(O_2)] to be seen by e.s.r. investigation. In conclusion it must be remembered that, while the reaction of [Co(pc)] with O_2 was quite unknown, the analogous reaction of tetrasulphophthalocyaninatocobalt(II), [Co(tspc)], was already known; [31] [Co(tspc)] was oxygenated in a methanol solution with gaseous NH_3. In the light of these results, it is believed that the differences in reaction conditions between [Co(pc)] and [Co(tspc)] only arise through the different solubilities of the two complexes.

We thank Dr. P. Gerbaz of L.S.R. SNAM Progetti for thermal analyses and the Italian C.N.R. for support.

[4/238 *Received, 7th February*, 1974]

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[27] M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1971, 2720; S. Bruckner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1969, **3**, 308.

[28] H. A. O. Hill, J. M. Pratt, and R. J. Williams, *Discuss. Faraday Soc.*, 1969, **47**, 165.

[29] H. A. Harper, 'Review of Physiological Chemistry,' Lange Medical Publications, Los Altos, California, 1963.

[30] J. P. Contour, P. Lenfant, and A. K. Vish, *J. Catalysis*, 1973, **29**, 8.

[31] E. W. Abel, J. M. Pratt, and R. Whelan, *Chem. Comm.*, 1971, 449.