New Adducts of Phthalocyaninatocobalt(II) with Base Molecules. Part 3.† Chemical and Spectroscopic Relations between Mono (Low- and High-spin) and Bis Adducts

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New adducts of phthalocyaninatocobalt(II) with piperidine, 1-methylimidazole, 3,4-dimethylpyridine, 3,5-dimethylpyridine, 4-methylpyridine, 3-chloropyridine, pyrazine, 3-ethylpyridine, 4-ethylpyridine, 3-acetylpyridine, and 4-acetylpyridine have been synthesized. Strong σ-donor bases form bis adducts, while low σ ability favours the formation of mono adducts. All the bis adducts are low-spin species. Mono adducts may contain either low- or high-spin configurations. Apart from being favoured by the electronic properties of the base, the high-spin configuration is also favoured by steric hindrance and is probably accompanied by the exit of the cobalt atom out of the phthalocyaninato-plane. Electron spin resonance parameters provide evidence for the stabilization of the ^4E_g state on passing from bis to mono adducts and for the removing of axial symmetry on passing from low-spin to high-spin mono adducts. It is suggested that the ground state of the high-spin mono adducts derives from the ^4E_g state of the corresponding low-spin species.

RECENT advances in the chemistry of phthalocyaninatocobalt(II) [Co(pc)] [1-3] have been concerned with the electronic and structural variations related to: (i) the change of polymorphous form; (ii) the axial co-ordination of one or two base molecules; and (iii) the reactivity with molecular oxygen. One very significant result is concerned with the stability of the high-spin [Co(pc)-(3Me-py)] derivative (3Me-py = 3-methylpyridine).[2] This compound supports a more direct comparison between phthalocyaninato- and haem derivatives. Indeed its oxygen absorption reproduces the changes of the metal spin state observed in the haem proteins after oxygen co-ordination. This paper reports the synthesis, magnetic, and electronic properties of some new low-spin mono and bis adducts, and of high-spin mono adducts of [Co(pc)] with nitrogenous bases. The aim is to differentiate more accurately the co-ordinating properties of various base molecules and to investigate the axial perturbation favourable to the change in spin state of the cobalt.

TABLE 1

Conditions for the reaction of β-[Co(pc)] with base molecules; analytical data and magnetic properties of the [Co(pc)]–base adducts

Base [a]	[Co(pc)] : base ratio	Reaction temperature (θ_c/°C)	Reaction time	Separation conditions	Magnetic behaviour [b]	Thermal dissociation range of base (°C)	Base (%) [c]		Metal (%)	
							Found	Calc.	Found	Calc.
pip	1 : 2	Variable	Variable	Variable	l.s.	120—180	22.7	22.9	7.80	7.95
mim	1 : 1	195	1 day	80 °C	l.s.[d]	186—210	11.8	12.5	8.95	9.00
	1 : 2	r.t.	7 days	r.t.	l.s.	140—180	21.8	22.3	7.80	8.00
3,4Me$_2$-py	1 : 1	160	3 h	r.t.	h.s.[e]	145—190	16.3	15.8	8.55	8.70
3,5Me$_2$-py	1 : 2	80—170	Variable	r.t.	l.s.	120—180	27.5	27.2	7.30	7.50
4Me-py [f]	1 : 1	145	45 min	100 °C	h.s.[e]	140—178	13.8	14.0	8.60	8.90
3Cl-py	1 : 1	148	2 h	80 °C; r.t.	l.s.[g]	120—180	16.5	16.5	8.45	8.60
pyz	1 : 1	54	1 day	r.t.	l.s.	180—220	11.7	12.3	8.75	9.05
3Et-py	1 : 1	80	1 h	80 °C	l.s.[d]	140—200	15.8	15.8	8.50	8.70
	1 : 2	r.t.	15 days	r.t.	l.s.	95—140	27.2	27.2	7.30	7.50
4Et-py	1 : 1	80	2 h	80 °C	l.s.	160—200	16.5	15.8	8.50	8.70
	1 : 2	80	2 h	r.t.	l.s.	85—145	26.1	27.2	7.30	7.50
3Ac-py	1 : 1	r.t.	2 days	r.t.	h.s.[e]	160—180	17.8	17.5	8.30	8.50
4Ac-py	1 : 1 + 1 : 2	Variable	Variable	Variable	l.s.					

[a] pip = Piperidine; 3,5Me$_2$-py = 3,5-dimethylpyridine; 4Me-py = 4-methylpyridine; 3Cl-py = 3-chloropyridine; pyz = pyrazine; 3Et-py = 3-ethylpyridine; 3Ac-py = 3-acetylpyridine; 4Ac-py = 4-acetylpyridine. [b] l.s. = Low-spin; h.s. = high-spin. [c] By thermal analysis. [d] Very low concentration of h.s. [e] Low concentration of l.s. [f] Obtained from the bis adduct. [g] Low concentration of h.s.

EXPERIMENTAL

Preparation of Compounds.—Preparation of all phthalocyaninatocobalt(II) adducts was carried out by treating β-[Co(pc)] (250 mg) with liquid base (5 cm^3) at temperatures and for reaction times which varied for different bases. Reaction temperature and the solubility of products were the object of a systematic investigation, since connections exist between these parameters and the properties of the isolated compounds. The experimental conditions used for the preparation of the complexes are in Table 1, together with their magnetic properties and thermal behaviour. The incomplete combustion of the complexes, usual in compounds of this type,[1,2] hindered reliable analyses of C, N, and H; however, the thermal gravimetric analysis results for the co-ordinated base and the good quality of cobalt analyses removed any doubt on the product stoicheiometry. The

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† Part 2 is ref. 2.

mono adduct of pyrazine was obtained by reacting β-[Co(pc)] (250 mg) in the fused base (5 g) for 1 d. The cold mixture was carefully washed with dimethyl ether to eliminate unreacted pyrazine. The high-spin form of the 4-methylpyridine mono adduct was obtained by refluxing the corresponding low-spin bis adduct in the base. The insoluble high-spin compound was filtered off at 100 °C.

Magnetic and Thermal Measurements.—Electron spin resonance spectra were recorded at room temperature on a Varian E9 spectrometer. The magnetic parameters were derived by standardization with diphenylpicrylhydrazyl. Thermal analyses were carried out on a Dupont 900 apparatus equipped with a Dupont 950 thermogravimetric analyzer, at a heating rate of 5 °C min^{-1} under a stream of nitrogen. Metal analyses were made with a Varian Techtron atomic-absorption spectrophotometer.

RESULTS

Magnetic Properties.—The magnetic properties of the adducts reported here were studied by e.s.r. spectroscopy alone, since mixing compounds with different spin states adversely affects magnetic susceptibility measurements. Resonances of both low- and high-spin compounds are clearly detectable at room temperature, on polycrystalline samples. In the case of the high-spin adducts, the evidence of signals at room temperature is surprising, as previously reported for the analogous compound with 3-methylpyridine. It is suggested (see later) that the large distortion of these high-spin compounds from cubic symmetry is the source of the anomalous behaviour. Indeed no examples of cobalt complexes with distortions of such magnitude are known. All the low-spin compounds show axial symmetry with $g_\perp$ values which distinguish between the mono and the bis adducts. Evaluation of the corresponding $g_\parallel$ values is more difficult. The values of the magnetic tensor components are shown in Table 2. In all the high-spin compounds a rhombic anisotropy was observed (Table 3). This rhombic distortion is clearly visible in the spectrum of [Co(pc)-(3,4Me$_2$-py)] (3,4Me$_2$-py = 3,4-dimethylpyridine) which is the purest high-spin mono adduct obtained up until now (see Figure 1). The high-spin adducts always appear to be mixed with variable amounts of the low-spin form, which is visible in the e.s.r. spectrum as a resonance at *g ca.* 2. Dilution of all the adducts reported here, both low- and high-spin, with [Zn(pc)] leads to low-spin mono adducts of [Co(pc)]. It is very probable that [Zn(pc)] interposes between the cobalt centres preventing the co-ordination of a second base molecule. The electronic identification of the ground state of low-spin adducts was attempted and for this purpose only the e.s.r. spectra of polycrystalline samples were considered. The g values in Table 2 are usual for compounds of this type. The ground state of [Co(pc)] and of its low-spin mono and bis adducts is, without any doubt,[1,2] $^2A_{1g}$ [derived from the $(x^2-y^2)^2(xz,yz)^4(z^2)$ strong-field configuration]. For compounds having a $^2A_{1g}$ ground state the principal g components can be expressed as a function of the mixing coefficients among the $^2A_{1g}$ state, the ^2E_g state [derived from the $(x^2-y^2)^2(xz,yz)^3(z^2)^2$ configuration], and the ^4E_g state [derived from the $(x^2-y^2)^2(xz,yz)^3(z^2)(xy)$ configuration] which couple by spin–orbit interaction.[4] By using the expressions $g_\parallel = 2.0023 + 2c_3{}^2 - 3c_1{}^2$ and $g_\perp = 2.0023 + \frac{2}{3}c_3{}^2 - 6c_1{}^2 + 6c_1$ where $c_1 = \zeta/[E(^2E_g) - E(^2A_{1g})]$, $c_3 = \zeta/[E(^4E_g) - E(^2A_{1g})]$, and ζ = spin–orbit coupling constant of cobalt, we calculated the relative contributions of the doublet ^2E_g and the quartet ^4E_g states to the ground Kramer's doublet. Precise data are not given by the spectra of polycrystalline powders, although they allow us to differentiate the adducts of various bases. Therefore we tried to reproduce the order of energy levels calculated for β-[Co(pc)], [Co(pc)(4Et-py)], and [Co(pc)(4Et-py)$_2$] (4Et-py = 4-ethylpyridine) by means of e.s.r. and ligand-field spectra (see Figure 2). The high-spin complexes reported here have magnetic parameters very similar to those reported for the high-spin complex [Co(pc)(3Me-py)].[2] Even for the high-spin adducts reported in this paper the resonances observed are related to the $|+\frac{1}{2}\rangle \longleftrightarrow |-\frac{1}{2}\rangle$ transition and the spectrum can be interpreted in terms of a fictitious $S' = \frac{1}{2}$ spin Hamiltonian. The large tetragonal distortion of all the base adducts of [Co(pc)] supports this assignment. Moreover, the large rhombic distortion observed in high-spin compounds sug-

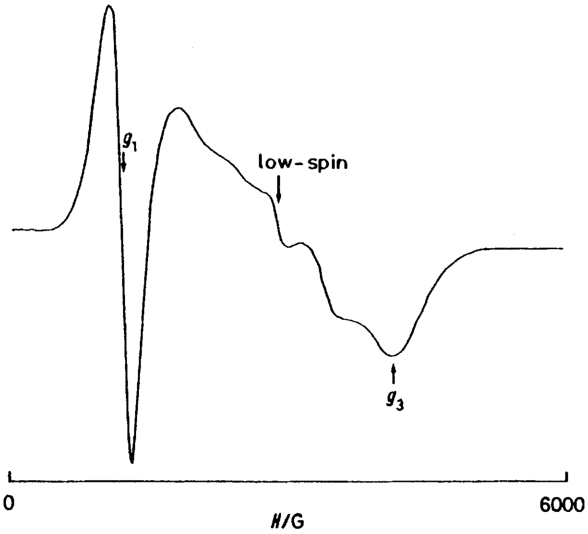


FIGURE 1 E.s.r. spectrum of a polycrystalline sample of [Co(pc)(3,4Me$_2$-py)] recorded at room temperature

TABLE 2

E.s.r. parameters of low-spin complexes

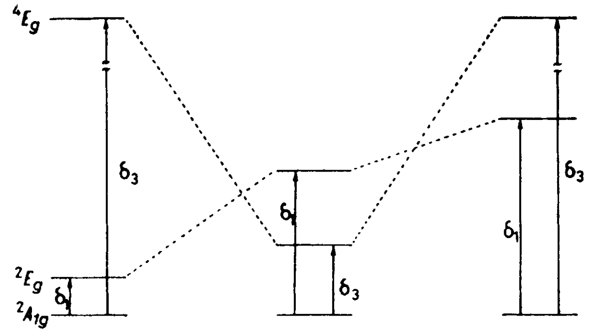
Adduct	$g_\perp$	$g_\parallel$
[Co(pc)(3Et-py)]	2.28	2.04
[Co(pc)(3Et-py)$_2$]	2.22	2.00
[Co(pc)(4Et-py)]	2.31	2.04
[Co(pc)(4Et-py)$_2$]	2.22	2.00
[Co(pc)(3,5Me$_2$-py)$_2$]	2.22	2.01
[Co(pc)(mim)]	2.31	2.02
[Co(pc)(mim)$_2$]	2.25	2.00
[Co(pc)(pip)$_2$]	2.23	2.00
[Co(pc)(pyz)]	2.29	2.02

TABLE 3

E.s.r. parameters of the high-spin complexes [Co(pc)(base)]

Base	g_1	g_2*	g_3
4-Methylpyridine	5.56	*ca.* 2	1.53
3-Acetylpyridine	5.94	*ca.* 2	1.58
3-Ethylpyridine	5.68	*ca.* 2	1.52
3,4-Dimethylpyridine	5.59	*ca.* 2	1.58
3-Chloropyridine	4.75	*ca.* 2	1.65
1-Methylimidazole	4.60	*ca.* 2	1.43

* The g_2 value is difficult to estimate, because of the presence of signals from the low-spin mono adducts in the same region.



	β-[Co(pc)]	[Co(pc)(4Et-py)]	[Co(pc)(4Et-py)$_2$]
c_1	0·19 (ref. 4)	0·05	0·04
c_3	0·01 (ref. 4)	0·15	0·01
δ_1(cm^{-1})	2100	7840 (7750)*	10610
δ_3(cm^{-1})	40000	3770	40000

FIGURE 2 Energy-level scheme of the low-spin compounds calculated by means of e.s.r. parameters (ζ = 400 cm^{-1}). * Experimental value from electronic reflectance spectrum (see ref. 1)

gests that the orbital degeneracy of the cobalt ground state is removed and that the e.s.r. spectrum at room temperature is mainly due to an orbital singlet ground state. In the absence of single-crystal analysis the assignment of the g components is doubtful. However the large contribution of the ^4E_g state to the ground state of the low-spin mono adducts (see Figure 2) suggests that one of the orbitally non-degenerate states derived from the splitting of the ^4E_g state becomes the ground state of the high-spin compounds.

Reactivity towards Oxygen.—The co-ordination of molecular oxygen by [Co(pc)(base)] in solution was described in previous papers.[1,2] These new phthalocyaninato-adducts also displayed reactivity towards oxygen in base–CH_2Cl_2 mixed solutions, and the results are similar to those reported in Part 1.[1] Different behaviour, with respect to the usual reactivity, was shown by the mono adduct containing 1-methylimidazole (mim). From the solution of the refluxed β-[Co(pc)] (250 mg) in 1-methylimidazole (5 cm^3), a blue powder precipitated after 3 d. In its e.s.r. spectrum, shown in Figure 3, as well as the signals of low-spin and high-spin mono adducts, the resonances of a new species also appear. The resonance field (g *ca.* 2.01) suggests that the new species has radical properties, but the amplitude of the signal and its asymmetric shape lead us to propose that the O_2^- radical anion, interacting with [Co(pc)(mim)], could be the new paramagnetic species. The signal is narrower than those of the analogous [Co(pc)(base)(O_2)] adducts, characterized by solution studies. Thus, we cannot make a complete analogy between the superoxide adducts usually displayed by the oxygen carriers and the present compound, but strong similarities seem evident.

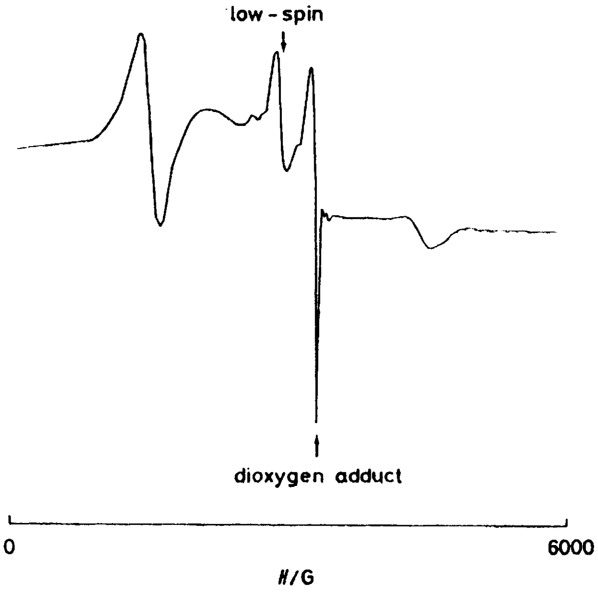


FIGURE 3 E.s.r. spectrum of 1-methylimidazole derivatives and their dioxygen adducts

DISCUSSION

Although general correlations between the properties of the co-ordinated base, reaction conditions, and type of isolated product cannot be made, it has been observed that (i) in the most favourable cases, when low-spin mono and bis adducts of the same base were isolated, the reaction temperature and solubility control the number of co-ordinated base molecules. The reaction carried out at room temperature, over a long period of time, always favours the formation of bis adducts; if an equilibrium exists between the mono and bis adduct, room temperature shifts the equilibrium in the bis adduct direction. Reactions carried out at high temperature favour the formation of the mono adduct.

(ii) Both the steric and electronic properties of the co-ordinated base influence the formation of either a mono or bis adduct. If one considers the bases which yield only one product, the 1 : 1 or the 1 : 2 adduct, it seems that strong σ donors favour bis adduct formation (see, for example, piperidine) while weak σ donors stabilize the mono adduct (*e.g.* pyrazine). This behaviour can be explained by the order of the energy levels shown in Figure 2. On passing from [Co(pc)] to the mono and bis adduct, the weight of the $(x^2 - y^2)^2(xz,yz)^3(z^2)^2$ configuration decreases in the ground state. In fact when additional ligands co-ordinate in axial positions with respect to the phthalocyaninato-plane, the energy of the d_{z^2} orbital increases and, if the axial ligand has empty π^* orbitals, the energy of the $d_{xz,yz}$ orbitals decreases. In conclusion, a large energy difference between the $^2A_{1g}$ and ^2E_g states stabilizes the bis adduct, hence an axial ligand which is a strong σ donor is a necessary condition for bis adduct formation. The energy-level scheme in Figure 2 also shows that the weight of the ^4E_g state in the ground Kramer's doublet is higher in the mono adducts than in the bis adducts. This suggests that the cobalt centre is out of the phthalocyaninato-plane in the mono adducts. In reality, displacement of a metal out of the phthalocyaninato-plane leads to an energetic stabilization of the d_{xy} orbital, increasing the weight of the $(x^2-y^2)^2(xz,yz)^3(z^2)(xy)$ configuration in the ground state. On this basis, it may be proposed that significant steric hindrance of the axial base favours the exit of cobalt out of the phthalocyaninato-plane and stabilizes the mono adduct (see, for example, 3-chloropyridine, 3-acetylpyridine, and 3,4-dimethylpyridine). The behaviour of 3,5-dimethylpyridine remains unexplained. Far i.r. data[5] are also in agreement with the displacement of cobalt. Moreover, deviations of the phthalocyaninato-complexes from planarity are well known and examples of such structures are provided by phthalocyaninatotin(II),[6] phthalocyaninatolead(II),[7] phthalocyaninatobis(pyridine)magnesium(II) monohydrate,[8] and by the adduct of phthalocyaninatozinc(II) with n-hexylamine.[9]

(iii) The $(x^2 - y^2)^2(xz \text{ or } yz)^2(yz \text{ or } xz)(z^2)(xy)$ configuration, which is stabilized on passing from the complexes of bis to mono adducts, very likely becomes the ground state of the high-spin complexes; this explains why only the mono adducts can take the high-spin cobalt configuration. In consequence, the properties of the base which stabilize mono adduct formation also favour stabilization of high-spin cobalt. The $(x^2 - y^2)^2(xz \text{ or } yz)^2(yz \text{ or } xz)(z^2)(xy)$ ground-state configuration, having one of the unpaired electrons in the d_{xy} orbital, supports the hypothesis that the high-spin complexes are characterized by a large displacement of cobalt out of the phthalocyaninato-plane. Far-i.r. data[5] confirmed that in a series of adducts of the same base the degree of cobalt displacement followed the order: high-spin mono adduct > low-spin mono adduct > bis adduct. However, a large deviation from planarity is not a sufficient condition for high-spin stabilization, since the electronic properties of the base must also have some influence.

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