New Adducts of Phthalocyaninatocobalt(II) with 3-Methylpyridine and Pyridazine and their Vibrational, Magnetic, and Electronic Properties. Part II. High-spin Adducts

By **Franco Cariati** and **Franca Morazzoni**, Istituto di Chimica Generale ed Inorganica dell'Università, Via Venezian 21, Milano, Italy
Carlo Busetto, L.S.R. Snam Progetti, San Donato Milanese (Milano), Italy

The tendency to six co-ordination and the strength of the intermolecular interaction in phthalocyaninatocobalt(II) are discussed with reference to the properties of its adducts with 3-methylpyridine and with pyridazine. The various spin states of (3-methylpyridine)phthalocyaninatocobalt(II) strongly resemble those found in the haem group on changing the axial ligand.

PREVIOUS work [1] on adducts of phthalocyaninatocobalt(II), [Co(pc)], with bases (pyridine and 4-methylpyridine) left unresolved some questions, of which the principal two are: (*i*) what is the relation between five- and six-co-ordination, when the equatorial ligand is a porphyrin-like molecule; and (*ii*) what is the strength and the origin of the intermolecular interaction in the polymorphous forms of [Co(pc)]. Both questions may be related to the biochemical problem concerning the role of the ligands at the fifth and sixth co-ordination sites in the haem group, and the influence of the co-ordination symmetry of Fe^{II} on the reactivity towards oxygen. Knowledge of the electronic properties of the new adducts reported in this paper could contribute to the clarification of these problems since the changes in spin state strongly resemble the various spin states found in haemoglobin and myoglobin haem on changing the axial ligands.

EXPERIMENTAL

Instrumentation.—Vibrational spectra were recorded on a Perkin-Elmer 621 spectrophotometer, and electronic spectra on a Beckman DK 2A spectrophotometer. Magnetic measurements were made by the Gouy method. E.s.r. spectra were recorded with a Varian 4502-11 spectrometer and the *g* values were measured by standardisation

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[1] F. Cariati, D. Galizzioli, F. Morazzoni, and C. Busetto, *J.C.S. Dalton*, 1975, 556.

with diphenylpicrylhydrazyl. Thermal analyses were made on a Dupont 900 apparatus, equipped with a Dupont 950 thermogravimetric analyser, at a heating rate of 1 °C min^{-1} under a stream of nitrogen at 40 $\text{cm}^3\ \text{s}^{-1}$. Metal analyses were made with a Varian Techtron atomic-absorption spectrophotometer.

Syntheses of Complexes.—*(3-Methylpyridine)phthalocyaninatocobalt*(II), [Co(pc)(3-Mepy)]. A suspension of β-[Co(pc)] in 3-methylpyridine was heated under reflux for *ca.* 3 h and then filtered to separate the unchanged β-[Co(pc)]. After a short time, a blue microcrystalline solid precipitated. Elemental and thermal analyses showed that the new complex is the mono adduct with 3-Mepy (Found: Co, 8.60; 3-Mepy, 14.0. Calc.: Co, 8.90; 3-Mepy, 14.0%). The base molecule is lost between 120 and 160 °C. A complex of identical stoicheiometry was synthesised by suspending β-[Co(pc)] in 3-Mepy at room temperature for 15 d. The product was a blue amorphous powder, and the base was lost between 130 and 180 °C.

Phthalocyaninatobis(pyridazine)cobalt(II), $[\text{Co(pc)(pdz)}_2]$. On heating β-[Co(pc)] under reflux in pyridazine solution the bis adduct was formed. It was necessary to filter the hot solution in order to remove unchanged β-[Co(pc)]. The complex $[\text{Co(pc)(pdz)}_2]$ was precipitated at room temperature. The reaction with pyridazine was slower than with the other bases, and the yields were low. Elemental and thermal analyses were in accordance with the stoicheiometry $[\text{Co(pc)(pdz)}_2]$ (Found: Co, 7.90; pdz, 21.0. Calc.: Co, 8.05; pdz, 21.9%). Both pyridazine molecules were lost between 90 and 140 °C. Attempts to prepare $[\text{Co(pc)(pdz)}_2]$ by suspending [Co(pc)] in pyridazine at room temperature were unsuccessful.

The synthesis of adducts of [Co(pc)] with other bases, such as quinoline and aniline, was attempted and, although there was evidence that the molecules could co-ordinate, pure compounds could not be isolated. In fact, large amounts of β-[Co(pc)] were always present in the final products. As explained in the Discussion section, the electronic and steric factors are probably opposed in these cases.

RESULTS

Magnetic Properties.—Both polymorphous forms of [Co(pc)] are low-spin complexes,[2] as usually required by a planar geometry for Co^{II}. All the mono and bis adducts described in Part I were tetragonal low-spin complexes. That the co-ordination of bases generally does not change the spin state of the parent complexes, α- or β-[Co(pc)], is confirmed by the adduct $[\text{Co(pc)(pdz)}_2]$ for which μ = 2.52 B.M. at room temperature.* On the other hand [Co(pc)(3-Mepy)], obtained under reflux in the base, showed a magnetic moment value μ *ca.* 3.05 B.M. at room temperature, which is anomalous for a tetragonal low-spin complex. This value increased on increasing the time for which the adduct remained in its mother liquor at room temperature, until, after 15 d of stirring, it gained a stable value, characteristic of high-spin cobalt(II) complexes. An identical high-spin magnetic moment was shown by [Co(pc)(3-Mepy)], obtained from the same reaction at room temperature, after stirring for 15 d. Clearly, two magnetically different forms of [Co(pc)(3-Mepy)] exist, high and low spin, of which the former is the more stable. However, it was not possible to completely remove the low-spin complex from the above mixture (see e.s.r. results). The magnetic-susceptibility values for the high-spin complex, from 289 to 85 K, are given in Table 1, and a plot of these results is shown in Figure 1. The shapes of the curves are difficult to explain, either as the magnetic behaviour of tetragonal high-spin Co^{II} (which is generally complicated by spin–orbit coupling effects and distortion [3,4]) or as a small amount of low-spin complex. The magnetic-susceptibility values do not obey the Curie–Weiss law, as expected for a mixture of complexes with different spin states, and the values decreased sharply with decreasing temperature. It is suggested that the ground state of the high-spin complex has a large contribution from an orbital singlet and the low energy of this singlet with respect to the other states could explain the decreasing μ value with temperature.

TABLE 1

Molar-susceptibility and magnetic-moment values of [Co(pc)(3-Mepy)], from 85 to 289 K. The values refer to one cobalt centre and have been corrected for the diamagnetism of the ligands

T/K	85	96.5	104	116.5	128
$10^6\chi_{\text{corr.}}$/c.g.s. units	14 240	12 414	11 956	11 704	11 584
μ/B.M.	3.11	3.09	3.15	3.56	3.45
T/K	138	148	158	168	180
$10^6\chi_{\text{corr.}}$/c.g.s. units	11 478	11 339	11 206	11 086	10 987
μ/B.M.	3.56	3.65	3.76	3.86	3.97
T/K	190	205	217.5	227	237
$10^6\chi_{\text{corr.}}$/c.g.s. units	10 900	10 701	10 661	10 622	10 628
μ/B.M.	4.07	4.18	4.31	4.39	4.48
T/K	255	265	274	289	
$10^6\chi_{\text{corr.}}$/c.g.s. units	10 469	10 436	10 376	10 343	
μ/B.M.	4.63	4.70	4.77	4.89	

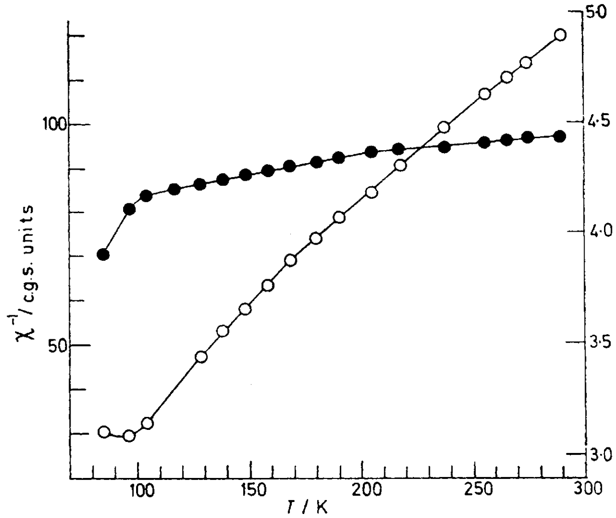

FIGURE 1 Variation of the magnetic-susceptibility (●) and magnetic-moment values (○) with temperature for the [Co(pc)(3-Mepy)] complex

The e.s.r. investigation on powdered [Co(pc)(3-Mepy)]

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* 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

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

[3] M. Gerloch and P. N. Quested, *J. Chem. Soc.* (*A*), 1971, 3729; M. Gerloch, P. N. Quested, and R. C. Slade, *ibid.*, p. 3741.

[4] C. Stoufer, D. W. Smith, E. A. Clevenger, and T. E. Norris, *Inorg. Chem.*, 1966, **5**, 1167.

confirmed the results of the magnetic-susceptibility measurements. The complex obtained from the reaction at the reflux temperature of 3-Mepy had an e.s.r. spectrum [Figure 2(*a*)] with resonance lines at low and medium field, the lines at medium field being much stronger. The adduct obtained at room temperature had an identical spectrum [Figure 2(*b*)], but the intensity ratios were inverted compared with the spectrum in Figure (2*a*). The resonance lines at medium field (g 2.42) are characteristic of low-spin [Co(pc)] adducts with bases [1] and all the other lines may be ascribed to a high-spin cobalt complex, having a strong tetragonal distortion and significant rhombic anisotropy (g_1 5.55, g_2 2.78, and g_3 1.54). The resonance lines of both low- and high-spin complexes were clearly detectable at room temperature and showed unexpected resolution for a high-spin complex. This behaviour confirms that the ground state of the high-spin form has no orbital degeneracy, as expected for a rhombic field symmetry. In the absence of single-crystal analysis, the ground-state configuration may be only tentatively assigned, the choice being between $(xy)^2(xz$ or $yz)^2(yz$ or $xz)(z^2)(x^2 - y^2)$ and $(xy)(xz)^2(yz)^2(z^2)(x^2 - y^2)$.[5] The first alternative showed the best fit with the experimental g values, on assigning g_1 to the out-of-plane component of the magnetic tensor and g_2 and g_3 to the in-plane components. This conclusion is also in agreement with the energy-level diagram previously reported for the low-spin base adducts of [Co(pc)]; [1] this makes the energy of $(xy) < (xz,yz) < (z^2) < (x^2 - y^2)$. The dilution of high-spin [Co(pc)(3-Mepy)] with [Zn(pc)] led to complete disappearance of the high-spin resonance lines and to conversion of the product into the low-spin bis adduct, [Co(pc)(3-Mepy)$_2$]. The bis adduct cannot be obtained as a solid, but has now been found diluted in a mixed powder, as it was also found in the solution of 3-Mepy.[6] It may be concluded that the high-spin complex cannot be stabilised when the cobalt centres are diluted.

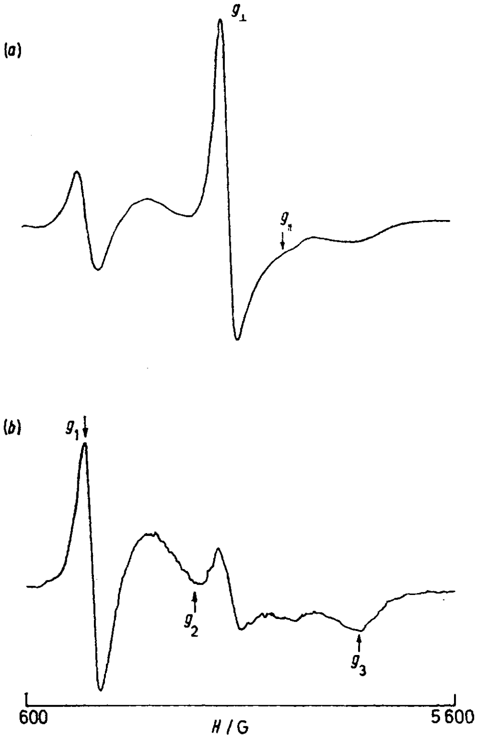

FIGURE 2 E.s.r. spectrum at 77 K of [Co(pc)(3-Mepy)] synthesised (*a*) at the reflux temperature of 3-Mepy and (*b*) at room temperature

Electronic and Vibrational Properties.—The i.r. spectra of both the 3-methylpyridine and pyridazine adducts were recorded in the region between 850 and 700 cm^{-1}. As described in Part I, this range of wavenumbers may be easily compared with the analogous region in the spectra of α- and β-[Co(pc)]; moreover, it may support the discussion of the different molecular packings between α- and β-[Co(pc)], and their adducts with bases. The absorption bands in this region are in Table 2. The skeletal vibrations of the phthalocyaninato-ligand in [Co(pc)(3-Mepy)] are quite similar to those of α-[Co(pc)], much more so than were the bands of [Co(pc)(py)] (py = pyridine). For [Co(pc)(pdz)$_2$], the similarity is between the bis adduct and β-[Co(pc)].

TABLE 2

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

Complex	
[Co(pc)(3-Mepy)]	803w,* 772m, 753s, 724vs
[Co(pc)(pdz)$_2$]	802w,* 779m, 753s, 734vs
α-[Co(pc)]	771m, 755s, 722vs
β-[Co(pc)]	780m, 755s, 733vs

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

* Due to co-ordinated base.

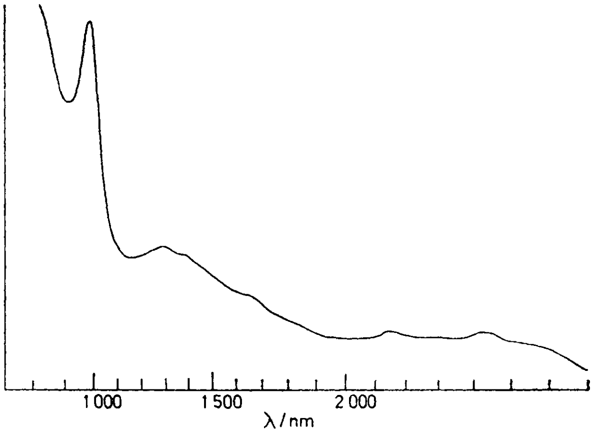

FIGURE 3 Electronic-reflectance spectrum of [Co(pc)(3-Mepy)]

The electronic-reflectance spectra of both [Co(pc)(pdz)$_2$] and [Co(pc)(3-Mepy)] were very similar and clearly show, when compared with those of α- and β-[Co(pc)], that the planar ligand field has been strongly perturbed by the base (Figure 3). The most interesting feature is in the spectrum of [Co(pc)(3-Mepy)] which, if compared with those of the other base adducts, shows an additional broad band at *ca.* 1 300 nm (*ca.* 7 700 cm^{-1}). This band may be reasonably assigned to the high-spin form of [Co(pc)(3-Mepy)] and would correspond to the one-electron transition d_{xz} or $d_{yz} \rightarrow d_{z^2}$

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[5] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.*, 1951, **A206**, 173; J. S. Griffith, 'The Theory of Transition-metal Ions,' Cambridge University Press, 1961, p. 360.

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

or to the transition $d_{xy}\rightarrow d_{z^2}$. Calculations made by Ciampolini[7] showed that the energies of these transitions are not very different.

DISCUSSION

In the syntheses of the [Co(pc)] adducts with pyridine and 4-methylpyridine, the formation of the two possible products was dependent on the temperature and the bis adducts were shown to be the more stable.[1] The reaction of [Co(pc)] with 3-methylpyridine gave only the mono adduct whatever the reaction temperature, whereas the reaction with pyridazine gave only the bis adduct. It is possible to conclude that the strength of the base determines the choice between the mono and bis adducts, as the stronger the base the more stable is the mono adduct; the co-ordination of the fifth ligand has an electronic effect which destabilises the sixth *trans*-ligand. In the case of [Co(pc)(3-Mepy)], the electronic effects are more favourable to five-co-ordination and oppose the tendency of the phthalocyaninato-ligand to a planar arrangement, with the cobalt atom lying in the centre of this plane. A possible way in which [Co(pc)(3-Mepy)] can attain the minimum distortion of the planar ligand would be dimerisation of two mono adducts. It is suggested that the cause for the slow change in the spin state of [Co(pc)(3-Mepy)] is a dimerisation process, which makes the cobalt ion six-co-ordinate in a rhombic crystal field.

The magnetic and e.s.r. measurements on these complexes may be satisfactorily explained by considering that, when the synthesis is carried out at high temperature, a large amount of monomeric mono adduct is present compared with a small amount of dimer; after a long time, the conversion to the dimer is almost complete. On the other hand, it could be suggested that the high- and low-spin complexes are different spin forms of the same monomeric mono adduct in thermal equilibrium.[8] The first suggestion is at present favoured because, if the change in spin state were not a consequence of a different ligand field around the cobalt, it would be possible to vary the ratio of the high-spin to the low-spin complex only by varying the temperature, and e.s.r. spectra of samples derived from the reactions at various temperatures (or the related magnetic-moment values) would be identical if measured at the same temperature. This was not the case and it is concluded that the ratio of the high-spin to the low-spin complex is dependent on the temperature of reaction with 3-Mepy.

Dimerisation of [Co(pc)(3-Mepy)] certainly cannot occur through metal–metal interaction, because this would produce a diamagnetic complex. The most obvious possibility is that a cobalt atom of [Co(pc)(3-Mepy)] co-ordinates to a nitrogen of the planar ligand of another [Co(pc)(3-Mepy)] complex. An intermolecular interaction of this type, although not so strong as to change the spin state, was also suggested in the cases of [Co(pc)(py)] and α-[Co(pc)], on the basis of their vibrational and thermal properties.[1] In the present case, since the spectrum of the mono adduct with 3-Mepy is quite coincident with that of α-[Co(pc)] and very similar to that of [Co(pc)(py)] in the i.r. region, diagnostic of intermolecular interaction[9] (see Table 2), it is suggested that the order of interaction is [Co(pc)(3-Mepy)] $\gg$ [Co(pc)(py)] > α-[Co(pc)] > β-[Co(pc)].

The formation and the magnetic characterisation of a high-spin metal phthalocyaninato-complex is an interesting problem, either from a strictly chemical point of view or in the light of the biochemical implications. The phthalocyaninato-ligand, as with all porphyrin-like molecules, has never been found to stabilise high-spin complexes; clearly the rigidity of this ligand favours a planar arrangement or, in the case of six-co-ordination, a highly distorted octahedral symmetry with a stronger field in the equatorial plane. In both this and the previous paper it is shown that the co-ordination of a base in the fifth position or of two molecules of base maintains the spin state of the parent complex [Co(pc)]; it may be that the simultaneous presence of a molecule of strong field in the fifth position and of a molecule of weak field in the sixth position (the phthalocyanine nitrogen of another molecule) changes the cobalt spin state. The electronic arrangement of dimeric [Co(pc)(3-Mepy)] strongly reproduces the field which stabilises the high-spin state in haem group of haemoglobin and myoglobin.[10] These iron(II) complexes, which have one strong-field ligand, imidazole, in the fifth co-ordination position, are in a high-spin state when the sixth position is occupied by a low-field ligand (*e.g.* water). Replacement of the weak-field ligand by one of strong field converts the respiratory proteins into low-spin (diamagnetic) complexes (oxyhaemoglobin and oxymyoglobin).

In a similar way, the present high-spin cobalt(II) complex [Co(pc)(3-Mepy)] achieves the low-spin electronic arrangement when the sixth position is occupied by a strong-field ligand, *e.g.* in 3-Mepy solution and on dilution with [Zn(pc)]. An analogous change of spin state has been observed on reaction with oxygen: [Co(pc)(3-Mepy)], in accordance with its dimeric structure, is completely insoluble in organic solvents, but, when suspended in tris(dimethylamino)phosphine oxide, it gives quantitatively the soluble oxygen adduct [Co(pc)(3-Mepy)(O_2)], a paramagnetic low-spin complex having e.s.r. parameters common to all similar oxygen adducts.[11]

Cobalt(II) phthalocyaninate, in the light of the arguments reported in Part I and this paper, shows the minimum tendency to distortion of the planar ligand, and, when the electronic conditions favour five-co-ordination, the molecule prefers to dimerize. The

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[7] M. Ciampolini, *Structure and Bonding*, 1969, **6**, 52.

[8] R. C. Stoufer, W. B. Hadley, and D. H. Bush, *J. Amer. Chem. Soc.*, 1960, **82**, 3487.

[9] D. N. Kendall, *Analyt. Chem.*, 1953, **25**, 382; A. A. Ebert, jun., and H. B. Gottlieb, *J. Amer. Chem. Soc.*, 1952, **74**, 2806.

[10] M. Weissbluth, *Structure and Bonding*, 1967, **2**, 1.

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

properties of the α form of [Co(pc)] may be also considered to indicate its tendency to packing. As regards the electronic state of the metal, [Co(pc)] is the only porphyrin-like complex to resemble the spin state of the natural iron(II) complexes, on co-ordination of one 3-Mepy molecule. The reaction of oxygen with all the base adducts of [Co(pc)] was a substitution process, never an addition; the substitution process is that most probably involved in oxygen absorption by the haem proteins.

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