Co-ordination Bond Properties in Phthalocyaninatometal(II) Complexes. Part 1. Stereochemistry and Bond Properties in Bis(4-methylpyridine)-phthalocyaninatometal(II)–4-Methylpyridine (1/2) (Metal = Cobalt or Iron)

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A comparison between the vibrational properties and stereochemistry of [Co(pc)(4Me-py)$_2$] and [Fe(pc)(4Me-py)$_2$] [pc = phthalocyaninato(2 –), 4Me-py = 4-methylpyridine] is carried out by using far-i.r. spectroscopy and *X*-ray diffractometry. The crystals of the two complexes, based on the packing of [M(pc)(4Me-py)$_2$] adducts and solvated 4Me-py molecules, are isostructural and their orthorhombic unit cells (space group *Pbca*) have the following parameters: M = Co, *a* = 10.395(1), *b* = 25.069(3), *c* = 17.992(2) Å, 1 503 unique observed reflections, final *R* 0.061; M = Fe, *a* = 10.315(1), *b* = 25.006(3), *c* = 17.876(2) Å; 2 950 unique observed reflections, final *R* 0.063. All the findings lead to the conclusion that structural results and bond properties are strictly related in these complexes. The vibrational M–N(pc) parameters are much more affected than the corresponding structural parameters by differences in the electronic structures of cobalt and iron. In the case of axial M–N(4Me-py), however, the bond length depends strongly on the metal and its value (2.322 Å for M = Co and 2.040 Å for Fe) is a clear indication of the localization of the unpaired electron in the d_{z^2} orbital of the cobalt complex. The importance of $d\pi \rightarrow \pi^*$(pc) back donation is shown by the significant difference between the average values of the ' internal ' and ' external C–N bond lengths in the macrocycle.

RECENTLY the electronic properties of the central metal atom in phthalocyaninatocobalt(II) [Co(pc)] and in its adducts with base molecules have been investigated[1-3] with a special interest in the following topics: (*i*) the difference between the ligand fields of α- and β-[Co(pc)]; (*ii*) the variations in the electronic properties of cobalt induced by axial co-ordination of one or two base molecules; and (*iii*) the relation between the ligand-field properties and the oxygen-carrier function of cobalt. It seems now useful to extend this investigation by comparing the stereochemistry and the bond properties of this type of complex, in order to rationalize the dependence of the strength of the M–N bonds and of the phthalocyaninate internal bonds on the various electronic configurations.

A difficulty in this kind of study is the fact that the α forms of [M(pc)] and the monoadducts with base molecules show no tendency to form crystals of sizes suitable for *X*-ray diffraction analysis, thereby hindering direct knowledge of important structural details in many cases. We will start by establishing a correspondence between diffractometric results and spectroscopic data for phthalocyaninatometal adducts. Then, in a subsequent paper[4] the spectroscopic data obtained will be used to provide stereochemical information in cases where *X*-ray studies are not available.

Here we report the refined crystal structures and far-i.r. data for adducts with 4-methylpyridine, [M(pc)(4Me-py)$_2$] (M = Co^{II} or Fe^{II}), and compare directly their stereochemistries and bond properties. A brief account of a low-precision *X*-ray structural analysis of the iron complex has been published,[5] and we have reported[6] a preliminary ill-defined crystal structure of the cobalt adduct.

EXPERIMENTAL

Preparation of the Complexes. Bis(4-*methylpyridine*)-*phthalocyaninatometal*(II)–4-*Methylpyridine* (1/2), [M(pc)(4Me-py)$_2$]·2(4Me-py) (M = Co^{II} *or* Fe^{II}).—Both complexes were obtained as microcrystalline powders following literature methods.[7,8] Thermal analysis indicated that cleavage of both 4Me-py molecules from the two adducts occurs simultaneously. Dissociation temperatures range from 100 to 140 °C for M = Co and from 180 to 220 °C for M = Fe.

For the preparation of crystals of [Co(pc)(4Me-py)$_2$] suitable for *X*-ray analysis a solution was first obtained by refluxing the microcrystalline powder (100 mg) in 4Me-py (50 cm^3) with stirring; then the solution was slowly cooled to 40 °C and filtered. Slow evaporation (15 d) of this solution at a controlled temperature (40 °C) yielded light blue hexagonal crystal platelets of thickness <0.01 mm. Single crystals of [Fe(pc)(4Me-py)$_2$] were obtained by heating the microcrystalline powder (50 mg) in 4Me-py (50 cm^3) at 140 °C. The resulting hot solution was cooled to 40 °C and the microcrystalline precipitate, after filtration at 40 °C, yielded several red-purple hexagonal crystals, showing a size of 2—3 mm in the plane of the platelet and an average thickness of *ca.* 0.5 mm.

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Spectroscopic and Thermal Measurements.—Infrared spectra were recorded on Perkin-Elmer 621 and FIS 3 spectrophotometers. Thermal analyses were carried out on a Dupont 990 apparatus equipped with a Dupont 951 thermogravimeter analyser at a heating rate of 20 °C min^{-1} under a stream of nitrogen (40 cm^3 min^{-1}).

Crystal Data.—Both crystals were orthorhombic, with space group *Pbca*; Mo-K_α radiation (λ 0.710 69 Å). $C_{56}H_{44}CoN_{12}$, $M = 944$, $a = 10.395(1)$, $b = 25.069(3)$, $c = 17.992(2)$ Å, $U = 4\,688.6(3)$ Å^3, $Z = 4$, $F(000) = 1\,964$, $D_c = 1.337$ g cm^{-3}, μ(Mo-K_α) = 4.38 cm^{-1}. $C_{56}H_{44}FeN_{12}$, $M = 941$, $a = 10.315(1)$, $b = 25.006(3)$, $c = 17.876(2)$ Å, $U = 4\,610.9(3)$ Å^3, $Z = 4$, $F(000) = 1\,960$, $D_c = 1.355$ g cm^{-3}, μ(Mo-K_α) = 3.95 cm^{-1}.

X-*Ray Diffraction Measurements*.—For both randomly orientated crystals the intensities were measured (using graphite-monochromatized Mo-K_α radiation) on a Philips PW 1100 four-circle automatic diffractometer by the ω—2θ scan technique and by averaging two background counts for each reflection, with a background time of 2 × 10 s. The intensities I were considered observed when $I > 2.5\sigma$ (σ^2 = peak counts + total background counts). The other conditions are given in Table 1. Intensity data were corrected for Lorentz and polarization effects but not for absorption, in view of the small crystal size and absorption coefficient (μ). In the case of [Co(pc)(4Me-py)$_2$] the atomic positions were determined by the heavy-atom method, while [Fe(pc)(4Me-py)$_2$] was assumed to be isostructural with the cobalt complex on the basis of a comparison of the preliminary crystal data and of the intensity distributions. The crystal structures were refined by least squares, minimizing $\Sigma w(F_o - |F_c|)^2$ with unit weighting factors, in the block-diagonal approximation.* The atomic scattering factors given by Cromer and Mann [9] were used with constant corrections [10] for the Co and Fe atoms in order to account for the anomalous scattering. The thermal vibration parameters were refined isotropically at first and then anisotropically. Other details of the least-squares refinement, including the final values of the conventional R factor, are given in Table 1.

TABLE 1

Details of the crystallographic least-squares refinement

	[Co(pc)(4Me-py)$_2$]	[Fe(pc)(4Me-py)$_2$]
Scan speed/° s^{-1}	0.02(ω)	0.04(ω)
Scan width/°	1.00(ω)	0.80(ω)
Number of measured reflections	3 775	4 534
Crystal size/mm	0.45 × 0.40 × 0.01	0.37 × 0.27 × 0.48
Number of isotropic least-squares cycles	4	5
$R_{iso.}$*	0.122	0.114
Number of anisotropic least-squares cycles	5	5
$R_{aniso.}$*	0.061	0.063
Number of observed reflections ($I > 2.5\sigma$)	1 503	2 950

* $R = (\Sigma|KF_o - |F_c||)/\Sigma KF_o$, based on the observed reflections. Suffixes *iso* and *aniso* refer to the mode of refinement of the thermal vibration parameters (see text).

The refined atomic positional parameters and their estimated standard deviations are given in Tables 2 and 3 for [Co(pc)(4Me-py)$_2$] and [Fe(pc)(4Me-py)$_2$] respectively. Observed and calculated structure factors and thermal parameters for both crystals are listed in Supplementary Publication No. SUP 22266 (63 pp.).†

TABLE 2

Atomic positional parameters (× 10^5) for [Co(pc)(4Me-py)$_2$], with estimated standard deviations in parentheses *

	x/*a*	*y*/*b*	*z*/*c*
Co	00 000	00 000	00 000
N(1)	−16 543(41)	−533(20)	5 012(22)
N(2)	−5 880(43)	6 076(18)	−5 484(23)
N(3)	−27 641(43)	6 970(17)	−760(27)
N(4)	12 797(47)	8 095(17)	−12 903(24)
N(5)	6 974(46)	5 613(19)	9 368(25)
N(6)	−17 029(66)	24 986(27)	11 030(33)
C(1)	−26 832(57)	2 686(22)	3 783(28)
C(2)	−17 937(52)	8 435(21)	−5 142(29)
C(3)	−18 803(58)	12 970(22)	−10 168(27)
C(4)	−28 724(61)	16 488(25)	−11 767(35)
C(5)	−25 936(72)	20 363(25)	−17 094(34)
C(6)	−14 154(68)	20 696(23)	−20 601(32)
C(7)	−4 503(62)	17 129(22)	−18 940(31)
C(8)	−6 938(59)	13 266(21)	−13 656(29)
C(9)	882(63)	8 989(20)	−10 712(27)
C(10)	19 970(61)	4 291(21)	−10 099(29)
C(11)	33 325(55)	3 395(22)	−12 412(29)
C(12)	41 133(61)	6 009(23)	−17 499(30)
C(13)	53 687(58)	4 266(25)	−18 084(32)
C(14)	58 107(54)	−19(31)	−14 053(31)
C(15)	50 246(65)	−2 779(22)	−9 019(31)
C(16)	37 618(53)	−1 025(21)	−8 349(27)
C(17)	6 290(62)	4 253(24)	16 618(31)
C(18)	11 888(64)	6 998(25)	22 178(30)
C(19)	19 151(62)	11 510(24)	20 806(32)
C(20)	19 615(68)	13 048(24)	13 505(37)
C(21)	13 606(62)	10 113(24)	8 061(33)
C(22)	26 056(88)	14 453(31)	26 883(33)
C(23)	−17 665(73)	30 060(29)	9 199(39)
C(24)	−11 698(66)	32 248(27)	3 276(38)
C(25)	−3 912(56)	29 217(27)	−1 504(35)
C(26)	−3 377(72)	23 846(26)	361(49)
C(27)	−9 695(92)	22 038(31)	6 491(48)
C(28)	3 134(80)	31 425(32)	−8 086(44)

* N(5) and C(17)—C(22) belong to the co-ordinated 4Me-py; N(6) and C(23)—C(28) belong to the non-co-ordinated 4Me-py.

RESULTS AND DISCUSSION

Crystal Structures.—The crystals of the two complexes are isostructural. The structure is shown in Figure 1 and consists of four molecules of [M(pc)(4Me-py)$_2$] (M = Co or Fe) and eight molecules of non-co-ordinated 4-methylpyridine per unit cell. The metal atoms lie at the inversion centres at (0,0,0), ($\frac{1}{2}$,$\frac{1}{2}$,0), (0,$\frac{1}{2}$,$\frac{1}{2}$), and ($\frac{1}{2}$,0,$\frac{1}{2}$), while the solvated base molecules are close to the binary screw axes, which run parallel to the *a* crystal axis. As suggested by Figure 1, the structure can be described as a packing of interleaving layers of [M(pc)-(4Me-py)$_2$] molecules and of solvated base molecules parallel to the *ac* crystallographic plane. No intermolecular distance is less than the sum of the commonly accepted van der Waals radii.

The co-ordination polyhedron around M approximates to a tetragonal bipyramid with relatively long bonds

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* All the computer routines used here are part of a system of crystallographic programs written by A. Immirzi (version for the Univac 1108 computer).

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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between the metal atom and the axial base ligands. In both cases (M = Co and Fe) the metal and the four co-ordinated nitrogen atoms in the macrocycle lie on a plane, as imposed by the local crystal symmetry, while the dihedral angle between this plane and that containing the base ligands is slightly but significantly different from 90°. The most important structural details are presented in Table 4, where the lettering refers to the scheme in Figure 2.

TABLE 3

Atomic positional parameters (× 10^5) for [Fe(pc)(4Me-py)$_2$], with estimated standard deviations in parentheses. Details as in Table 2

	x/a	*y/b*	*z/c*
Fe	00 000	00 000	00 000
N(1)	−16 611(27)	−509(12)	5 007(15)
N(2)	−6 065(28)	6 175(11)	−5 461(15)
N(3)	−27 874(29)	7 020(11)	−620(17)
N(4)	13 016(29)	8 270(11)	−12 879(15)
N(5)	6 561(28)	4 865(11)	8 327(15)
N(6)	−17 542(47)	24 662(19)	11 384(25)
C(1)	−27 091(34)	2 790(13)	3 929(17)
C(2)	−18 022(35)	8 475(13)	−4 905(19)
C(3)	−19 046(38)	13 002(14)	−9 995(19)
C(4)	−28 963(41)	16 577(16)	−11 543(22)
C(5)	−26 397(47)	20 572(16)	−16 760(24)
C(6)	−14 532(48)	20 905(16)	−20 352(23)
C(7)	−4 605(43)	17 341(15)	−18 909(20)
C(8)	−7 023(37)	13 364(14)	−13 624(19)
C(9)	880(36)	9 062(13)	−10 666(18)
C(10)	20 129(34)	4 297(13)	−10 197(18)
C(11)	33 533(35)	3 438(14)	−12 482(19)
C(12)	41 595(40)	6 171(15)	−17 475(20)
C(13)	54 213(40)	4 356(17)	−18 131(22)
C(14)	58 696(37)	−3(18)	−14 077(22)
C(15)	50 618(39)	−2 776(15)	−9 198(20)
C(16)	37 903(35)	−1 028(14)	−8 516(19)
C(17)	4 885(37)	3 684(14)	15 625(19)
C(18)	9 965(41)	6 634(16)	21 357(20)
C(19)	17 132(41)	11 184(16)	19 901(21)
C(20)	18 421(45)	12 628(16)	12 365(23)
C(21)	13 187(39)	9 400(14)	6 899(21)
C(22)	23 383(62)	14 364(22)	26 037(27)
C(23)	−18 219(54)	29 842(21)	9 664(30)
C(24)	−12 208(47)	32 116(18)	3 664(28)
C(25)	− 4 769(45)	29 035(19)	−1 136(26)
C(26)	−3 857(51)	23 649(19)	699(30)
C(27)	−10 221(64)	21 649(20)	6 788(33)
C(28)	2 417(56)	31 330(23)	−7 630(31)

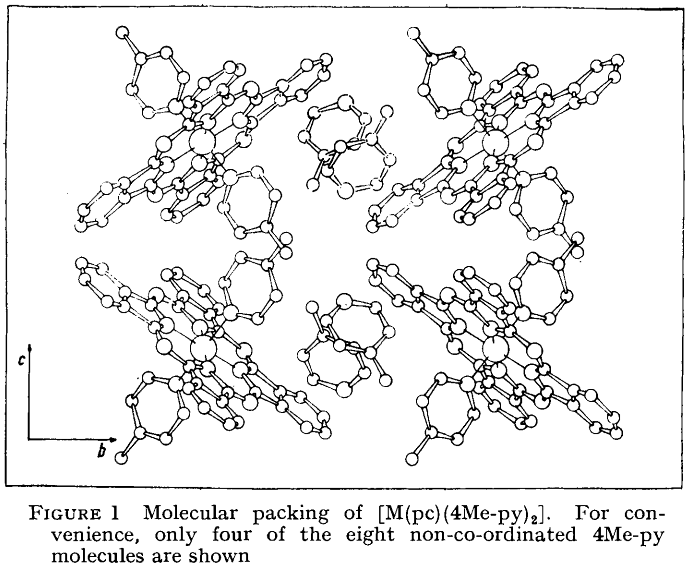

FIGURE 1 Molecular packing of [M(pc)(4Me-py)$_2$]. For convenience, only four of the eight non-co-ordinated 4Me-py molecules are shown

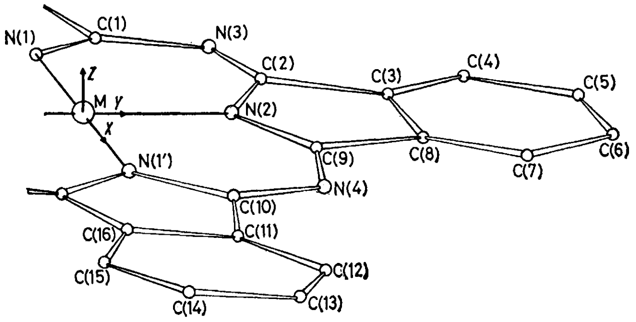

FIGURE 2 Scheme showing the molecular (*X*,*Y*,*Z*) reference system and the lettering used in the text

The main differences between the two structures are found: (*i*) in the axial metal–nitrogen (of the co-ordinated base) bond distance which is much larger when M = Co [2.322(5) Å] than Fe [2.040(3) Å]; and (*ii*) in the fact that when M = Fe the co-ordination geometry corresponds almost rigorously to a local D_{4h} symmetry, while when M = Co the deviation from this ideal situation is very significant [Co–N(1) 1.945(4), Co–N(2) 1.914(4) Å]. The long M–N(5) axial bond in [Co(pc)(4Me-py)$_2$] is probably due to the unpaired electron which is essentially localized in the d_{z^2} orbital of Co^{II}, as indicated by e.s.r. studies [2] on this base adduct and on α- and β-[Co(pc)]. Even larger distances have

TABLE 4

Selected bond lengths (Å) and angles (°) in the two complexes [M(pc)(4Me-py)$_2$], with estimated standard deviations in parentheses

	Co	Fe
M–N(1)	1.945(4)	1.937(3)
M–N(2)	1.914(4)	1.932(3)
M–N(5)	2.322(5)	2.040(3)
N(1)–C(1)	1.356(7)	1.373(4)
N(1′)–C(10)	1.361(7)	1.374(4)
N(2)–C(2)	1.387(7)	1.364(5)
N(2)–C(9)	1.389(7)	1.378(4)
N(3)–C(1)	1.358(7)	1.335(4)
N(3)–C(2)	1.328(7)	1.323(5)
N(4)–C(9)	1.331(8)	1.328(5)
N(4)–C(10)	1.320(7)	1.325(4)
C(2)–C(3)	1.447(7)	1.458(5)
C(8)–C(9)	1.440(8)	1.447(5)
C(10)–C(11)	1.459(8)	1.459(5)
C(1′)–C(16)	1.445(8)	1.452(6)
C(3)–C(4)	1.407(9)	1.386(6)
C(4)–C(5)	1.382(9)	1.391(6)
C(5)–C(6)	1.384(10)	1.385(7)
C(6)–C(7)	1.382(9)	1.379(6)
C(7)–C(8)	1.380(8)	1.397(5)
C(3)–C(8)	1.380(8)	1.400(5)
C(11)–C(12)	1.393(8)	1.396(5)
C(12)–C(13)	1.370(9)	1.381(6)
C(13)–C(14)	1.388(9)	1.386(6)
C(14)–C(15)	1.388(9)	1.392(6)
C(15)–C(16)	1.398(9)	1.387(5)
C(11)–C(16)	1.393(8)	1.400(5)
N(1)–M–N(2)	90.40(9)	89.95(6)
N(1)–M–N(5)	88.96(7)	89.68(5)
N(2)–M–N(5)	89.82(7)	89.98(5)

recently been observed by Little and Ibers [2.386(2) Å] [11] and by Scheidt [2.436(2) Å] [12] in similar complexes. Little and Ibers also calculated the Co^{III}–N(sp^2) bond distance, in the absence of electron localization in d_{z^2}, as 2.05 Å; therefore, in the case of [Co(pc)(4Me-py)$_2$] the axial bond lengthening, due to electron repulsion, is *ca.* 0.27 Å.

The deviation from D_{4h} symmetry observed in [Co(pc)(4Me-py)$_2$] is interesting also because it was not detected in the crystal of bis(3-methylpyridine)(2,3,7,8,12,13,17,18-octaethylporphinato)cobalt(II) [11] whose structure was determined with comparable accuracy. In the latter complex the Co–N(1) and Co–N(2) bond distances are identical and their value [1.992(1) Å] is larger than the average value (1.930 Å) calculated for [Co(pc)(4Me-py)$_2$]. In [Fe(pc)(4Me-py)$_2$] this average value (1.934 Å) is very close to 1.930 Å, but the two Fe–N(pc) bond distances are not significantly different from each other. It should be noted that also in the intermediate-spin complex phthalocyaninatoiron(II) [13] the local geometry about the Fe atom corresponds almost rigorously to D_{4h} symmetry and the average Fe–N(pc) distance (1.927 Å) is not significantly different from the value found here.

All the C–N and C–C bond distances in the two [M(pc)(4Me-py)$_2$] complexes are normal in the sense that their values are not very different from corresponding values found [14–16] in various metallophthalocyanines; however, the good accuracy of the present structure determinations and the relatively small standard deviations (especially for M = Fe) indicate that the differences between the average values of C–N(1) and C–N(2) [1.373(7) Å for M = Co and 1.373(6) Å for Fe] and the average values of C–N(3) and C–N(4) [1.334(7) Å for M = Co and 1.328(4) Å for Fe] are very significant. These differences indicate an accumulation of electron density on the outer carbons of the pyrrole rings and on the nitrogen bridge atoms and can therefore be explained by an important electron back donation from the metal d_π orbitals to the ligand $\pi^*(e_g)$ antibonding wavefunction, from which a maximum charge on those atoms can be calculated.[17,18] Also in crystals of β-[Fe(pc)] [13] the C–N outer distances (average 1.322 Å) were found to be smaller than the inner distances (average 1.378 Å), but no comment was made on this fact.

The orientation of the co-ordinated 4Me-py plane relative to a cartesian (X,Y,Z) reference system (Figure 2) attached to the macrocycle is fixed by the steric requirements imposed both by the conformation of the phthalocyanine ligand and by the positions of the solvated 4Me-py molecules in the structure. Indeed, any significant rotation of the 4Me-py ligand about the M–N(5) axis (approximately parallel to the Z axis) would reduce the non-bonding distances between carbon or hydrogen atoms of the axial ligand and atoms of the macrocycle and of solvated 4Me-py molecules below acceptable values, even when M = Co. In particular, a rotation of *ca.* 45°, making the axial-ligand plane parallel to the M–N(1) or M–N(2) bond directions (the X and Y axes of the reference system), would yield C–C non-bonding distances <3 Å and H–H distances <2 Å (some H–H distances would have values as low as 1.6 and 1.8 Å). It can be concluded that, in view of the particular orientation of the axial ligands, as imposed by steric hindrance from the structural environment, electron back donation from the metal d_{xz} and d_{yz} orbitals to the empty π^* orbitals of the 4Me-py ligands makes only a very small contribution, if any, to the axial bond. Optimization of the orbital overlap necessary to increase the importance of that contribution would require a reorientation of the axial-ligand plane from the observed position, approximately parallel to the M–N(4) direction, to a new position, parallel to the M–N(1) or M–N(2) directions, yielding unacceptable values of some non-bonding distances, as already pointed out. It is interesting to note that, contrary to the present evidence, optical-absorption and Mössbauer-resonance results [17] indicate the possibility of a significant contribution of electron back donation to the axial bond in these adducts.

Finally, we note that, while the internal MN_4 group is rigorously planar, the external part of the macrocycle significantly deviates from planarity, with the larger distortions observed in the benzene rings of [Co(pc)(4Me-py)$_2$].

Vibrational Properties.—The vibrational properties in the far-i.r. region can be easily related to the stereochemical features thereby giving direct information on the co-ordination bond strength of the complexes. Moreover, the vibrational analysis of this kind of complex is useful in itself, since no previous study has been reported of the vibration range involving the metal.

TABLE 5

Infrared spectra * (400—700 cm^{-1}) of phthalocyanine and phthalocyaninatometal(II) complexes

α-pc	685s, 675m, 615s, 555m, 490s, 435s, 425(sh)
β-pc	685s, 675m, 613s, 555w, 495m, 485(sh), 433s
β-[Zn(pc)]	685m, 675w, 638s, 572s, 498s, 435m
β-[Cu(pc)]	685m, 675w, 638s, 568s, 503s, 432s
β-[Mn(pc)]	650m, 567w, 505s, 430s
[VO(pc)]	668s, 642m, 637(sh), 570s, 505s, 440s
β-[Fe(pc)]	685m, 675w, 642s, 570s, 515s, 435s
β-[Co(pc)]	685m, 675w, 642s, 570s, 515s, 435s
β-[Ni(pc)]	685m, 675w, 642s, 572s, 520s, 435vs

* Nujol mulls; s = strong, m = medium, w = weak, and sh = shoulder.

This prompted us to consider the vibrational properties of the free ligand pc and of the complexes [M(pc)], before going on to examine the properties of the adducts with 4Me-py.

A comparison of the spectra of free phthalocyanine

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and of its complexes with various metal ions in the 100—700 cm^{-1} region (Tables 5 and 6 and Figures 3 and 4) shows that all the ligand bands are shifted to higher frequencies on complex formation. However, the absorptions are sensitive to the nature of the metal and to the symmetry properties of the chromophore MN_4 only in the 100—500 cm^{-1} region. The fact that the symmetry of the complex [VO(pc)] (C_{4v}) is lower than that of the other phthalocyaninatometal(II) complexes (D_{4h}) is paralleled by the splitting of several bands in the 100—400 cm^{-1} region (Figure 3). In conclusion, the highest sensitivity of the i.r. bands to the nature of the metal is shown by the metallophthalocyanines in the same region where it was observed for metalloporphyrins,[19] metallo-octaethylporphyrins,[20] metalloprotohaemins,[21] and similar complexes.

TABLE 6

Far-infrared spectra * (cm^{-1}) of phthalocyanine and phthalocyaninatometal(II) complexes

Compound	ν(M–N)	δ(NMN)	Other bands
α-pc			332m, 280m, 260m, 230w, 220m, 120m
β-pc			340m, 280m, 260m, 250(sh), 238m, 230m, 120m
β-[Zn(pc)]	256m	95vs	350w, 300w, 240m, 114s
β-[Cu(pc)]	284m	150vs	350w, 303w, 234w, 120s
β-[Mn(pc)]	290m	210vs	356w, 306m, 234w, 150w, 130w
[VO(pc)]	310w	180s	370m, 358m, 300w, 238w, 220w
	288w	170s	180s, 170s, 130w, 118m
β-[Fe(pc)]	308m	160vs	366w, 300m, 232w, 124s
		154(sh)	
[Fe(pc)(4Me-py)$_2$]	330s	160s	389w; 300s, 246m, 118m
β-[Co(pc)]	314s	172vs	372m, 302s, 240w, 122s
[Co(pc)(4Me-py)$_2$]	312s	172s	298m, 228w, 124m
		166(sh)	
β-[Ni(pc)]	318m	183s	376w, 300w, 232w, 122w

* In Polythene phase.

On these bases the M–N(pc) stretching vibrations and the (pc)N–M–N(pc) angular deformations of the [M(pc)] complexes have been assigned as in Table 6. This assignment is empirical, but the analogy with the one carried out by Ogoshi *et al.*[22] for isotope-substituted metallo-octaethylporphyrins makes it highly reliable. For the various metals, the trend with increasing ν[M–N(pc)] is $\mathrm{Zn^{II}} < \mathrm{Cu^{II}} < [\mathrm{VO}]^{2+} \approx \mathrm{Mn^{II}} < \mathrm{Fe^{II}} < \mathrm{Co^{II}} < \mathrm{Ni^{II}}$, similar to the trend for the same metals in octaethylporphyrins.

One possible explanation is that the occupancy of $d_\pi(d_{xz},d_{yz})$ orbitals, in the configuration giving the largest contribution to the ground state, increases from vanadium to cobalt. Indeed, in [Fe(pc)] [23] the ground-state configuration is predominantly $e_g^2b_{2g}^2a_{1g}^2$, and in β-[Co(pc)]^2 the main configuration is $e_g^4b_{2g}^2a_{1g}$. {The configuration $e_g^3b_{2g}^2a_{1g}$ cannot be excluded as the major contributor to the ground state in [Fe(pc)], in analogy with the case of [Co(pc)].^{2}} For [Ni(pc)] the ground-state configuration is predominantly $e_g^4b_{2g}^2a_{1g}^2$, while for the excited states one has to admit that the configuration $e_g^3b_{2g}^2a_{1g}^2b_{1g}$ in [Ni(pc)] is less important than $e_g^3b_{2g}^2a_{1g}^2$ in [Co(pc)].

The trend corresponding to the importance of d_π back donation, as obtained from i.r. data, is identical to the one obtained from electronic data,[18] with the energy of the $\pi(a_{1u})\rightarrow\pi^*(e_g)$ transition of the phthalocyaninate ligand strongly influenced by the electron back donation from the metal. Finally, the fact that the bond strength of the copper and zinc complexes is so low is probably due to the presence of electrons in the antibonding $d_{x^2-y^2}$ orbital; in fact, the bond strength is lowered by this effect more than it is increased by the occupation of d_π orbitals. The observed repulsion effect induced by the electrons in $d_{x^2-y^2}$ is in agreement with the results by Kirner *et al.*[13] on the intermediate-spin [Mn(pc)].

Specific comparisons between [Co(pc)] and [Fe(pc)] and their adducts [Co(pc)(4Me-py)$_2$] and [Fe(pc)(4Me-py)$_2$] are now made. In all these products one M–N stretching band (E_u) has been observed (Figure 4), in agreement with a D_{4h} symmetry of the chromophore. Co-ordination of 4Me-py lowers the symmetry to D_{2h} and two i.r.-active bands ($B_{2u} + B_{3u}$) should be expected. However, it is probable that the large axial bond length observed in both [Co(pc)(4Me-py)$_2$] and [Fe(pc)(4Me-py)$_2$] results in a reduction of the splitting of the E_u stretching band; apparently the difference of *ca.* 0.3 Å observed between the distances Co–N(Mepy) and Fe–N(Mepy) is not effective in this context. On the other hand, the (pc)N–M–N(pc) angular deformation is sensitive to small variations of symmetry and the observed difference between the angles N(1)–Co–N(2) and N(1′)–Co–N(2) in the cobalt adduct is in agreement with the splitting of the corresponding angular-deformation frequencies (see Figure 4). It is interesting to note that i.r. spectra indicate also that the angles N(1)–Fe–N(2) and N(1′)–Fe–N(2) are different in β-[Fe(pc)], while they give only a single unsplit band in [Fe(pc)(4Me-py)$_2$], where *X*-ray diffraction has shown that the two angles are identical. The angular anisotropy of [Fe(pc)] is in agreement with the structural results of Kirner *et al.*,[13] which confirm

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that the bending vibrational frequencies are more sensitive to structural changes than are stretching frequencies. We were not able to assign any band to the M–N(4Me-py) vibration which would be expected at <300 cm^{-1}, where the number of the free ligand bands (see Figure 3) is too high to allow assignment of M–N vibrations, which are probably very weak and coupled.

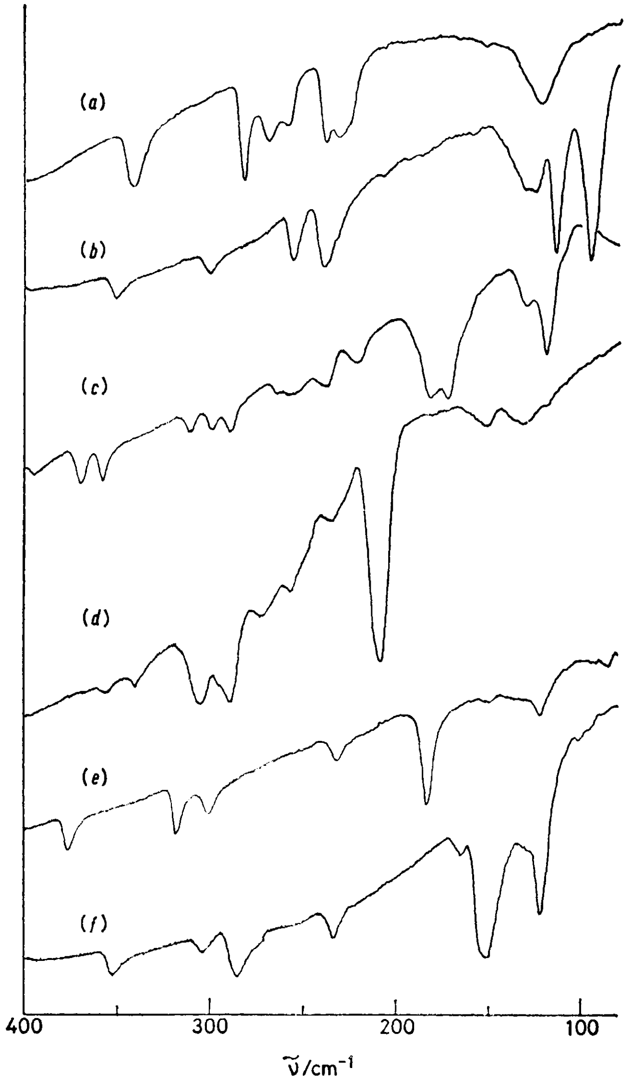

FIGURE 3 Far-infrared spectra (100—400 cm^{-1}) of free β-phthalocyanine (*a*) and of its metal complexes β-[M(pc)] [M = Zn (*b*), VO (*c*), Mn (*d*), Ni (*e*), or Cu (*f*)]

As for the ν[M–N(pc)] stretching vibrations, coordination of the axial bases strongly affects ν[Fe–N(pc)] while ν[Co–N(pc)] of β-[Co(pc)] and of [Co(pc)(4Me-py)$_2$] are almost the same (see Table 6). This behaviour can be easily explained by considering the ground-state configurations of the four complexes:

β-[Co(pc)]	$e_g^4b_{2g}^2a_{1g}$	(ref. 2)
[Co(pc)(4Me-py)$_2$]	$e_g^4b_{2g}^2a_{1g}$	(ref. 2)
β-[Fe(pc)]	$e_g^2b_{2g}^2a_{1g}^2$ (or $e^3b_{2g}^2a_{1g}$, see text)	(ref. 23)
[Fe(pc)(4Me-py)$_2$]	$e_g^4b_{2g}^2$	

The occupation of the e_g orbitals, to which back donation is due, increases from β-[Fe(pc)] to [Fe(pc)(4Me-py)$_2$] in agreement with the large shift of ν[Fe–N(pc)] to higher frequencies. This cannot be the case for β-[Co(pc)] and [Co(pc)(4Me-py)$_2$] which have identical ground-state configurations. The different electronic configurations also explain the differences in the M–N(pc) bond energy between [Co(pc)(4Me-py)$_2$] and [Fe(pc)(4Me-py)$_2$]. The contribution of the doublet excited configuration $e_g^3b_{2g}^2a_{1g}^2$ to the ground state of the cobalt complex is surely more important than that of the triplet excited configuration $e_g^3b_{2g}^2a_{1g}$ to the ground state of the iron complex, thus explaining the observed lower value of ν[M–N(pc)] in the cobalt adduct.

The vibrational data show that the electronic configuration is chiefly responsible for the variations in the M–N(pc) stretching frequencies of the two adducts. The mass differences must be of comparatively minor importance, otherwise the difference in the ν[M–N(pc)]

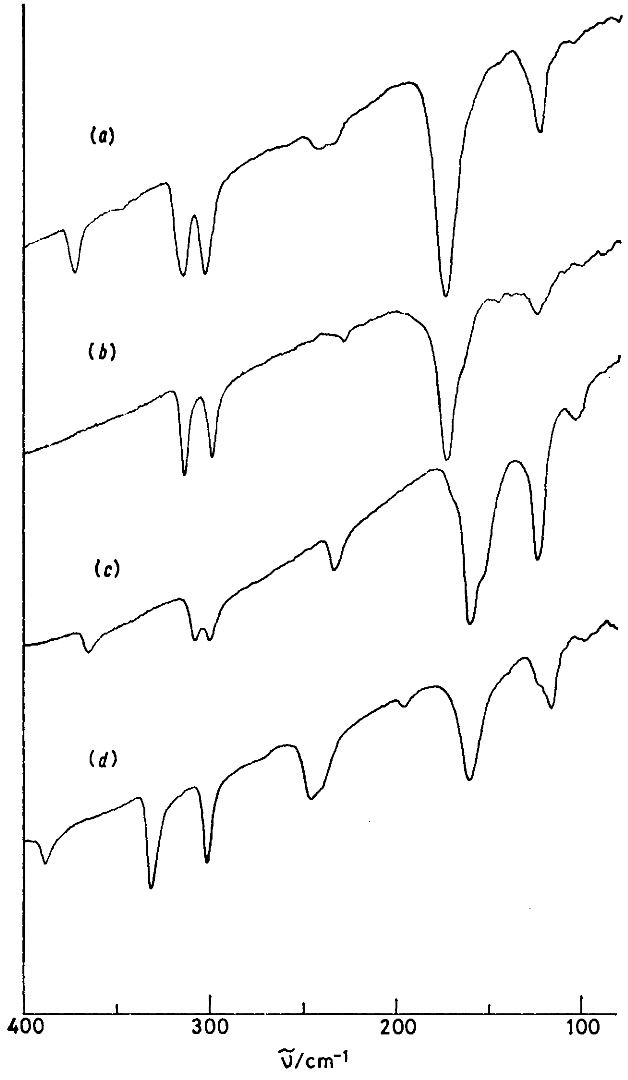

FIGURE 4 Far-infrared spectra (100—400 cm^{-1}) of β-[Co(pc)] (*a*), β-[Fe(pc)] (*c*), and of their adducts [Co(pc)(4Me-py)$_2$] (*b*) and [Fe(pc)(4Me-py)$_2$] (*d*)

frequencies between [Co(pc)(4Me-py)$_2$] and [Fe(pc)(4Me-py)$_2$] would be identical to that between β-[Co(pc)] and β-[Fe(pc)]. An analogous result follows from a comparison of the bending frequencies. It can be concluded that vibrational data can be correlated with structural data only if the metal electronic configuration does not change.

Conclusions.—The comparison between the structural results and the vibrational properties of [Fe(pc)(4Me-py)$_2$] and [Co(pc)(4Me-py)$_2$] leads to the following conclusions. (*i*) While the electronic and vibrational M–N bond properties in the plane of the phthalocyaninate anion are not very sensitive to differences in the corresponding M–N bond lengths, both the axial M–N(4Me-py) electronic bond properties and the corresponding distance are strongly dependent on the metal electronic state. The greater length of the M–N(4Me-py) bond for M = Co than for Fe, which is an obvious consequence of the occupation of the d_{z^2} orbital, is reflected in the thermal-dissociation temperature for 4-methylpyridine (see the Experimental section) in the two cases. As for the planar ligand, while the controlling factor of the bond length is the metal electronic structure, the geometry is determined by its stiffness. This stiffness is a particular property of this ligand; it is interesting to note that protohaemin complexes of iron show a distortion [12] from D_{4h} to D_{2h} local symmetry, due to a slight deformation of the planar ligand.

(*ii*) The effects of the $d_\pi \rightarrow \pi^*$(pc) electron back donation are clearly shown by the vibrational data and can be easily correlated to the stereochemical properties of the phthalocyaninate ligand. In [Co(pc)(4Me-py)$_2$] the $d_\pi(d_{xz},d_{yz})$ to $\pi^*(e_g)$ electron transfer is less important than in [Fe(pc)(4Me-py)$_2$], as is indicated by the fact that in the former complex, as compared with the latter, the N(1)–M–N(2) angle significantly deviates from 90°, the ν[M–N(pc)] vibration frequencies are lower, and the δ[(pc)N–M–N(pc)] vibrational band is split into two. Another effect of the $d_\pi \rightarrow \pi^*$(pc) electron back donation on the stereochemistry of the phthalocyaninate ligand is probably the significant difference between the average values of the 'internal' and 'external' C–N bond lengths in the macrocycle, as pointed out in the preceding section.

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