Spin Density and Cobalt Electronic Structure in Phthalocyaninatocobalt(II): A Polarised Neutron Diffraction Study

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The collection of polarised neutron diffraction data for β-phthalocyaninatocobalt(II), [Co(pc)] (Co^{II}, $S = \frac{1}{2}$), is described. Flipping ratios for 145 and 337 Bragg reflections were observed at 4.2 K and at magnetic field strengths of 1.49 and 4.6 T respectively. By use of the 4.2 K neutron diffraction nuclear structural data, these were converted into magnetic structure factors $F_M(hkl)$. A model of the spin distribution in [Co(pc)] was considered, employing the 3*d* and diffuse 4*s*-type orbitals of cobalt, and orbitals of the inner-ring nitrogen and carbon atoms of the ligand macrocycle. The spin populations of these orbitals were refined by a least-squares procedure which fitted calculated to observed magnetic structure factors. The spin populations $3d_{xy}^{0.40(10)}$, $d_{xz,\,yz}^{0.17(10)}$, $d_{z^2}^{0.79(12)}$, $d_{x^2-y^2}^{-0.21(10)}$, '$4s$'$^{-0.14(6)}$ were found, together with a total population of −0.17(5) spin on the macrocycle N and C atoms. The cobalt orbital *electronic* populations deduced are thus $3d_{xy}^{1.60}$, $d_{xz}^{1.83}$, $d_{yz}^{1.83}$, $d_{z^2}^{1.21}$, $d_{x^2-y^2}^{0.21}$ together with either '$4s$'$^{0.14}$ or '$4s$'$^{1.86}$. The above orbital populations, except for the d_{xy} case, are in reasonable concordance with knowledge of the electronic structure of the Co^{2+} ion, particularly when spin–orbit coupling is considered. However, the negative ligand spin densities which must arise through spin polarisation effects are in some conflict with the ^1H n.m.r. contact shift deductions. The magnetic moment per cobalt atom, along the *b* axis, $\langle\mu_b\rangle$, at 4.6 T, is determined to be 0.55 B.M. (1 B.M. = 9.274×10^{-24} A m^2).

THE electronic structure of square-planar cobalt(II) complexes has been the subject of extensive studies by various physical techniques, in particular because of the role of certain of them as reversible dioxygen carriers. One of the principal aims of the studies has been to establish the *d*-orbital energies, in order to see if correlations with O_2 bonding are obvious. Amongst the square-planar complexes of Co^{II}, the β-polymorph of phthalocyaninatocobalt(II), [Co(pc)], has been of special interest because, although not an O_2-carrier itself, it has obvious relationships to the porphyrin derivative and is of particular chemical stability and is very well characterised. The crystal structure of [Co(pc)] has been determined at 295 K by *X*-ray diffraction [1] and at 4.3 K by neutron diffraction.[2] The e.s.r. *g* values, $g_z = 1.9$, $g_\perp \sim 2.9$ are close to those of porphyrinatocobalt(II) compounds ($g_z \sim 1.8$, $g_\perp \sim 3.3$).[3] While some of the Schiff-base bivalent cobalt derivatives show well developed O_2-carrier properties, their *g* values are less similar [4] ($g_z \sim 1.9$, $g_x \sim 3.5$, $g_y \sim 1.8$) and chemically they are much less robust and are less well characterised than [Co(pc)].

The visible absorption spectra of square-planar cobalt(II) complexes do not reflect the *d*-orbital participation in the bonding at all well, as they are dominated by charge-transfer bands.[4] Prominence in the studies of the compounds has therefore been given to the magnetic properties such as magnetic susceptibility, anisotropy, and e.s.r.[5] There has been considerable discussion about the interpretation of the magnetic data in relation to the *d*-orbital energy separations, but recently clarification has come from more detailed considerations.[3,4] It is clear that in all the relevant compounds, the d_{z^2}, d_{xz}, and d_{yz} orbitals lie in a group very close in energy, well below the d_{xy} orbital, and with the $d_{x^2-y^2}$ orbital much higher again. The co-ordinate system used in this discussion is defined in Figure 1. The nomenclature of the group C_{2v} is adopted in order to facilitate comparison with the Schiff-base derivatives, although the approximate symmetry of [Co(pc)] is higher, D_{4h}. The co-ordinate system has been rotated by $\pi/4$ relative to that which has sometimes been used to discuss the properties of Schiff-base bivalent cobalt compounds.[4] The ground states of the complexes are not primarily the obvious ones, $^2B_2$ of the configuration $d_{xz}^2, d_{yz}^2, d_{z^2}^2, d_{xy}^1$, but rather on account of interelectronic repulsions, closer to $^2A_2$ with $d_{xz}^2, d_{yz}^1, d_{z^2}^2, d_{xy}^2$ for the Schiff-base compounds or $^2A_1$ with $d_{xz}^2, d_{yz}^2, d_{z^2}^1$, d_{xy}^2 for [Co(pc)] and porphyrinatocobalt(II) derivatives. The participation of the 4*s* orbital in the ground configuration by mixing, in particular with the d_{z^2} orbital, also of A_1 symmetry, has been suggested.[4]

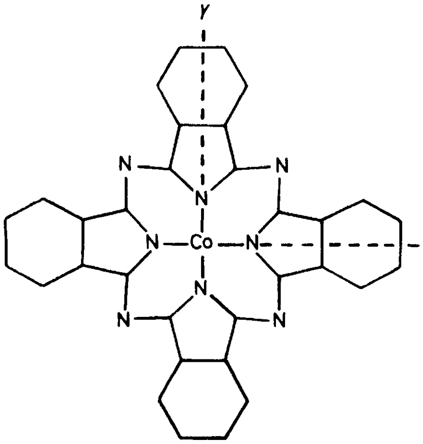

FIGURE 1 Schematic representation of the approximately planar [Co(pc)] molecule. The *X* and *Y* axes of the co-ordinate system used in this discussion are indicated; the *Z* direction is perpendicular to the CoN_4 plane. Unlabelled atoms are carbons

Although the members of the d_{z^2}–d_{xz}–d_{yz} set lie close together relative to interelectronic repulsion effects,

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to first order the $^2A_2$ or $^2A_1$ ground terms deduced correspond to the ' pure ' configurations written, so that fractional *d*-orbital populations are not involved. However, if the three *d* orbitals are so close in energy that their separations are not large compared with the spin–orbit coupling constant ζ_{3d}, this is no longer the case. The detailed analysis of the origin of the *g* values and principal magnetic susceptibilities of the square-planar compounds of cobalt(II) may be used to deduce corresponding *d*-orbital populations which are, in general, non-integral. The existence of such non-integral *d*-orbital populations may be investigated by the technique of polarised neutron diffraction (p.n.d.). We have in hand a program to study chemically significant compounds using the technique of p.n.d.,[6] and it has been demonstrated that, in suitable open-shell systems, p.n.d. can yield directly spin populations of individual *d* and possibly also of *s* and *p* atomic orbitals.[7,8] The first compound for which a comprehensive set of p.n.d. data was obtained was $Cs_3[CoCl_4]Cl$.[9] These data have been analysed in terms of the electronic configuration of the Co^{II} centre, and the degree of covalency (spin delocalisation) in the $CoCl_4^{2-}$ ion.[8] [Co(pc)](Co^{II}, $S = \frac{1}{2}$) is suitable for study by the p.n.d. technique because it remains a paramagnet at 4.2 K, with Curie–Weiss behaviour over the temperature range 4.2 to 295 K ($\theta = -3.2$ K).[10,11]

However, [Co(pc)] is considerably larger than any molecule yet studied by this technique. The major problem caused by the size of the molecule is the need to obtain a large amount of data of sufficient accuracy. At present the only facility providing the necessary high neutron flux and equipment for such an experiment is the Institut Laue-Langevin, Grenoble.

This paper describes the application of the p.n.d. experiment to the β-polymorphic form of [Co(pc)], and indicates the degree to which a p.n.d. experiment, using existing technology, can be successfully applied to chemical systems as large as the metallophthalocyanines. An analogous study has been performed on [Mn(pc)], and will be published later.[12]

EXPERIMENTAL

Large single crystals of the β-polymorphic form of [Co(pc)] suitable for p.n.d. studies, grown by entrainer vacuum sublimation techniques,[13] were made available by Dr. P. E. Fielding of the University of New England. The crystal data were taken from the 4.3 K neutron-diffraction structure determination:[2] $C_{32}H_{16}CoN_8$, $M = 571.48$, space group $P2_1/c$, $Z = 2$, $a = 1.449\,5(5)$, $b = 0.474\,2(4)$, $c = 1.910\,7(5)$ nm, $\beta = 120.76(2)°$. Polarised neutron diffraction ' flipping ratios '[9,14,15] were obtained at 4.2 K on the D3 normal-beam diffractometer located at a thermal neutron beam of the Institut Laue-Langevin high-flux reactor. The maximum flux available at the sample was *ca.* 3×10^{10} neutrons m^{-2} s^{-1}. Two data sets were obtained at different times on two different crystals at different magnetic field strengths. In both cases, 14 days use of the D3 diffractometer was available for data collection.

The first experiment was performed in order to explore whether useful p.n.d. data could be obtained from a $S = \frac{1}{2}$ *paramagnet*, especially one the size of the [Co(pc)] molecule. The crystal was approximately $1.0 \times 1.5 \times 15$ mm, with the largest dimension coincident with the *b* axial direction. The *b* axis of the crystal was aligned with the ω—2θ diffractometer axis, and a magnetic field of 1.49 T was applied along this direction. ' Flipping ratios ' (ratios of up-neutrons to down-neutrons) were obtained at λ 98.6 pm, with a small number also measured at λ 80.0 pm to check whether extinction effects were present. In general, 30 min were spent on each measurement and for many Bragg reflections the accessible symmetry equivalents were also measured. Only those *hkl* reflections with moderate to large *nuclear* intensities were measured, as the weaker reflections required much greater measuring times for worthwhile statistical accuracy. 326 Flipping ratios were measured at λ 98.6 pm, within the limits $0 < (\sin\theta)/\lambda \leqslant 5.03$ nm^{-1} and $k \leqslant 2$; of these, there were 197 distinct equivalences. The polarisation ratio, *P*, was 0.949 3(3) and flipping efficiency, *E*, was 1.000 0(3). Corrections for the polarisation and flipping efficiencies were made and the flipping ratios were converted to γ values by use of previously detailed formulae,[15] where $\gamma(hkl) = F_M(hkl)/F_N(hkl)$ is the ratio of magnetic $[F_M(hkl)]$ and nuclear $[F_N(hkl)]$ structure factors. Distinct equivalent $\gamma(hkl)$ values were combined, yielding 149 unique non-equivalent observations. The agreement index $A = \Sigma$ average $(|\gamma - \gamma_{av.}|)/\Sigma|\gamma_{av.}|$ was 0.186 for 48 pairs of equivalent reflections, where $\gamma_{av.}$ is the relevant mean intensity of a unique observation. The standard deviation in each γ value, $\sigma(\gamma)$, was determined from counting statistics. Phased F_M values, on absolute scale (B.M. unit $cell^{-1}$),* together with standard deviations $\sigma(F_M)$, were obtained from the γ and $\sigma(\gamma)$ values by use of F_N values calculated for a hypothetical extinction-free crystal from the 4.3 K nuclear structure refinement of [Co(pc)].[2] The $\sigma(F_M)$ values include an estimate (0.2 B.M. $cell^{-1}$) of the least-squares error in F_N which arises from errors in the structural model used to calculate F_N.

In this first experiment with *H* 1.49 T, 67 flipping ratios were also measured at λ 80.0 pm [*P* 0.921 4(9), *E* 1.000 0(9)], and identical reflections were averaged to give 15 unique observations. Because of the significantly lower neutron flux at this wavelength, these data were not as precise as those at λ 98.6 pm, and they were not used in subsequent analyses of the data. However, the agreement between these 15 data and the identical reflections measured at λ 98.6 pm indicated that, within the precision of the measurements, extinction effects were insignificant. The agreement index $\{\Sigma[(F_M - F_{av.})^2/\sigma^2(F_M)]/\Sigma[F_M{}^2/\sigma^2(F_M)]\}^{\frac{1}{2}}$ was 0.046 for the 15 pairs of identical reflections, where the summations are over all 30 individual observations of F_M, and $F_{av.}$ is the relevant mean magnetic structure factor.

The experimental average magnetic moment ($\langle\mu\rangle = \sigma_M/N\beta$ where σ_M is the molar magnetisation) for [Co(pc)] at 4.2 K is 0.272 B.M. per molecule at 1.7 T and 0.753 B.M. at 5.0 T.[11] These values are to be compared with 1.08 B.M. per CrF_6^{3-} ion in the p.n.d. experiment on $K_2Na[CrF_6]$ at 1.76 T,[7,14] and 3.6 B.M. per $CoCl_4^{2-}$ ion in the p.n.d. experiment on $Cs_3[CoCl_4]Cl$ at 4.6 T.[8,9] It is clear that the precision of a p.n.d. experiment is proportional to the magnetisation available. Therefore, although the magnetisation of a single [Co(pc)] crystal mounted about the *b* axial direction has not been measured, the above bulk magnetisation values confirm that the initial 1.49 T p.n.d. data obtained for [Co(pc)] should be very considerably less precise than the

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* Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2.

p.n.d. experiments on $K_2Na[CrF_6]$ and $Cs_3[CoCl_4]Cl$. In orderto obtain more precise [Co(pc)] p.n.d. data, a second experiment was performed using the same conditions described above, but with an applied field of 4.6 T.

A crystal of dimensions 0.7 × 1.0 × 15 mm was mounted with its b (needle) axis parallel to the applied magnetic field. Flipping ratios were obtained at λ 89.3 pm, and again only those Bragg reflections with moderate to large nuclear intensities were measured. 550 Flipping ratios were obtained [with P 0.967 4(3) and E 1.000 0(3)], within the limits $0 < (\sin\theta)/\lambda \leqslant 7.03$ nm^{-1} and $k \leqslant 2$; of these, there were 432 distinct equivalences. These were converted to γ values as before. Distinct equivalent $\gamma(hkl)$ values were combined, yielding 342 unique non-equivalent observations. The agreement index, A, was 0.149 for 90 pairs of equivalent reflections. Values of F_M were obtained as above. In this second 4.6 T data set, all reflections measured at 1.49 T were remeasured, and the data were extended further.

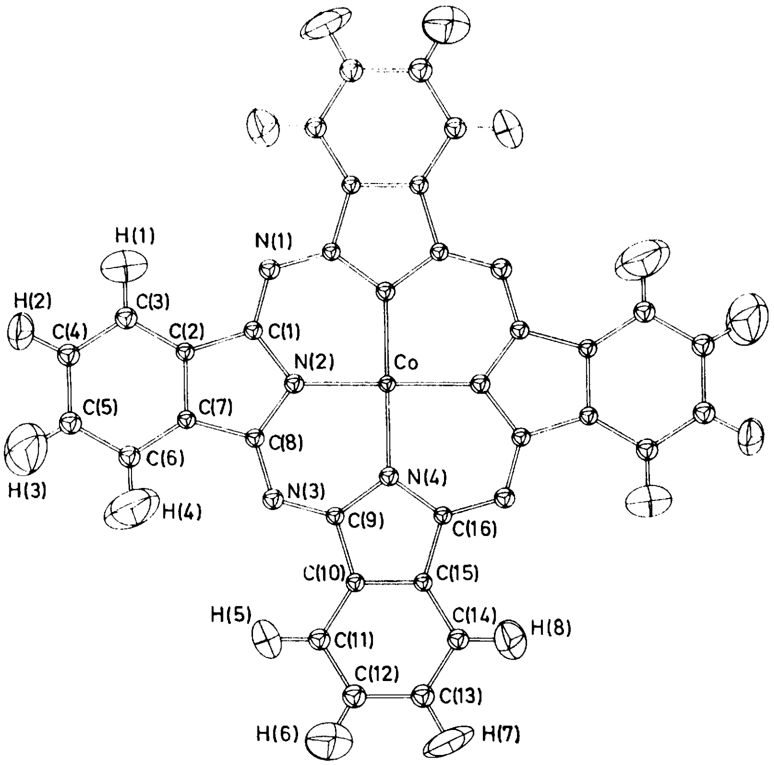

FIGURE 2 An ORTEP drawing of [Co(pc)] (4.3 K parameters) [2] showing the molecular geometry and atom numbering. The thermal ellipsoids are drawn at the 99% probability level

Modelling the Data.—The two sets of F_M data, obtained at 1.49 and 4.6 T, were not amalgamated although both are in principle related by a linear scale factor which is simply the ratio of the magnetisations at the two field strengths. They were treated separately because of the considerably greater precision of the 4.6 T data. The least-squares refinement program ASRED [16] was used to optimise the parameters in a chemically based modelling of the F_M data. In ASRED a set of quantisation axes is chosen, using chemical intuition and/or local symmetry for each atom. The spin populations of s, p, or d orbitals on each atom are then refined by a least-squares method. This procedure has been adequately described in detail elsewhere.[7,8,17]

Because [Co(pc)] is an essentially planar molecule, the z quantisation direction was chosen as perpendicular to the CoN_4 co-ordination plane for all atoms. For the Co atom, the x and y axes were chosen along the Co–N(2) and Co–N(4) bonds. The atom numbering and molecular geometry are shown in Figure 2. The model of the spin-density distribution in [Co(pc)] was restricted to a consideration of $3d$ orbitals, together with a spherically symmetrical diffuse $4s$-like orbital, on Co^{2+} and to $2p_z$ orbital populations on the inner ring ligand atoms N(1), N(2), N(3), N(4), C(1), C(8), C(9), and C(16). The quality of the data was not considered high enough to warrant any further degree of parameterisation of the model. In most refinements, based on the essential (although not crystallographic) D_{4h} symmetry of the [Co(pc)] molecule, the populations of the $3d_{xz}$ and $3d_{yz}$ orbitals were constrained to be equal.

Tabulated single-electron scattering factor curves for the $3d$ electrons of Co^{2+} and for the $2p$ electrons of neutral C and N were used.[18] The ' $4s$ ' scattering curve for Co^+ was calculated from a wave function with $\zeta = 2.0$,[19] using a published method.[20] Because such single-electron scattering curves apply to the theoretical free atom or ion, for real atoms in a chemical environment it is desirable to allow some expansion or contraction of the curve. This is accomplished in ASRED by a least-squares refinement of a radial parameter r, defined by $f(s) = f_0(rs)$ where $f(s)$ is the single-electron scattering factor at $(\sin\theta)/\lambda = s$ and $f_0(rs)$ is the free atom or ion scattering factor at $(\sin\theta)/\lambda = rs$. The refinement of r is associated with variation of the radial exponents of the atomic wave function.

A correction must be made for the orbital component of the magnetisation which contributes to F_M and which does not arise from the spin density. This orbital contribution arises from the mixing of orbitally degenerate higher states into the orbitally non-degenerate $^2A_1$ ground term by spin–orbit coupling. The dipole approximation [21] is used in ASRED to correct for the spherical component of the orbital contribution to F_M, in terms of the experimental g_b value [22] (2.50) and the theoretical form factor $\langle j_2 \rangle_{3d}$ for a free Co^{2+} ion.[18] This treatment assumes that the aspherical component of the orbital contribution is small enough that it can be neglected.

If an independent measurement is available of the magnetisation of the sample, at the same temperature and field strength, and aligned in the field along the same crystallographic axis, as for the p.n.d. experiment, then this value [as $F(000)$] can be used in ASRED to scale the structure factor calculation from the model. Because this value is not available for [Co(pc)], the spin populations from the refinements are on relative rather than absolute scale. They are presented below on absolute scale by assuming that essentially all of the spin density on the molecule has been accounted for in the model, and normalizing the summation of all spin in the model to the known value of one spin per [Co(pc)] molecule.

Because the phases of the magnetic structure factors are experimentally determined, the function minimised in the least-squares procedure is $\Sigma w(\Delta F)^2$ where $w = 1/\sigma^2(F_o)$ is the weight assigned to the F_o values, $\Delta F = F_o - F_c$, and F_o and F_c are the observed and calculated magnetic structure factors.

RESULTS

Variations of the model described above were refined using each of the 1.49 and 4.6 T data sets separately. They were also refined using both data sets together, keeping common *hkl* reflections separate and with a refineable scale parameter to place the 1.49 T data on the same magnetisation scale as the 4.6 T data. The results of the refinements are presented in Tables 1—3. In the modelling procedure, four reflections with $\sigma(F_M) > 0.3$ B.M. and five reflections with $\sigma(F_M) > 0.5$ B.M. were rejected from the 1.49 and 4.6 T data sets respectively. All the refinements mentioned in this discussion of the results were taken to convergence.

Of the agreement indices $R(= \Sigma|\Delta F|/\Sigma|F_o|)$, $R'\{=[\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}}\}$, and $\chi^2[=\Sigma w(\Delta F)^2/(n - v)]$, where n and v are numbers of observations and variables respectively, the goodness-of-fit, χ^2, is the most appropriate for indicating how well a particular model fits the data, within the experimental accuracy of the observations. The closer χ^2 approaches unity, the better the model fits the data. The conventional R index is in all cases relatively high, and is indicative of the low accuracy of much of the data, rather than of how well the various models fit the data. The index R_S $[=\Sigma\sigma(F_o)/\Sigma|F_o|]$ is 0.323 and 0.290 for 145 1.49 T and 337 4.6 T data respectively.

The simplest model attempted (Model 1, Tables 1—3) ignores any spin on the ligand atoms. The Co $3d$ and '$4s$' orbital populations from these refinements are on relative rather than absolute scale, because the net spin on the ligand, almost certainly non-zero, is ignored. The χ^2 values (Tables 1—3) indicate that this model, with all the spin density placed in cobalt-centred orbitals, fits the data reasonably well. However, the inclusion in the model of the provision for spin density in $2p_z$ orbitals centred on each of the inner-ring ligand atoms (Model 2, Tables 2 and 3) yields a significant improvement in the fit. By the imposition of as many constraints on the ligand $2p_z$ populations as is reasonable (Model 2, Table 1; Model 3, Tables 2 and 3), values for these populations of significant accuracy begin to emerge. Finally, refinements were attempted with the $3d_{xz}$, $3d_{yz}$, and $3d_{x^2-y^2}$ populations of Co fixed at zero (Model 3, Table 1; Model 4, Tables 2 and 3), as none of these populations was

TABLE 1

Orbital spin populations and agreement factors for spin-density distribution models of the [Co(pc)] molecule, based on 145 1.49 T data [a]

Centre [b]	Variable [c]	Model 1	Model 2	Model 3
Co	$3d_{xy}$	0.33(16)	0.55(23)	0.20(10)
	$3d_{xz}$, $3d_{yz}$	0.42(17)	0.48(24)	0
	$3d_{z^2}$	0.63(19)	0.81(28)	1.39(9)
	$3d_{x^2-y^2}$	−0.26(17)	−0.59(25)	0
	'$4s$'	−0.53(15)	−0.24(15)	−0.08(5)
	$r(3d)$	1.28(8)	1.11(7)	1.0
N(1)	$2p_z$	0	−0.05	−0.05
N(2)	$2p_z$	0	−0.05(1)	−0.05(1)
N(3)	$2p_z$	0	−0.05	−0.05
N(4)	$2p_z$	0	−0.05	−0.05
C(1)	$2p_z$	0	−0.03(1)	−0.03(1)
C(8)	$2p_z$	0	0.00(2)	0.00(2)
C(9)	$2p_z$	0	0.00	0.00
C(16)	$2p_z$	0	−0.03	−0.03
R		0.282	0.264	0.270
R'		0.163	0.138	0.142
χ^2		1.796	1.323	1.361
No. of variables		6	9	6
$F(000)_c$ (B.M. cell^{-1})		0.358	0.256	0.256

[a] A parameter which has been varied in the least-squares refinement is given an estimated standard deviation in brackets. Other parameters were either fixed at zero, or constrained to equal another variable, having the final value quoted. A negative spin population indicates spin density antiparallel to that of positive sign. [b] The Co, N, and C centres are at the positions and have the thermal parameters determined from the 4.3 K neutron diffraction structural analysis (ref. 2). [c] The symbols s, p, and d are used here to represent populations of the corresponding orbitals. Where two symbols appear on the one line, the population quoted refers to each orbital individually. The radial expansion parameter for the $3d$ orbitals, $r(3d)$, is defined in the text. For all other orbitals, r was fixed at unity. All orbital populations have been normalized to give one unpaired electron per [Co(pc)] molecule; in this process, the spin on the centrosymmetrically related ligand atoms has also been taken into account.

TABLE 2

Orbital spin populations and agreement factors for spin-density distribution models of the [Co(pc)] molecule, based on 337 4.6 T data *

Centre	Variable	Model 1	Model 2	Model 3	Model 4
Co	$3d_{xy}$	0.33(10)	0.37(11)	0.37(11)	0.32(6)
	$3d_{xz}$,$3d_{yz}$	0.16(10)	0.12(11)	0.12(11)	0
	$3d_{z^2}$	0.68(11)	0.78(13)	0.78(13)	0.92(4)
	$3d_{x^2-y^2}$	−0.11(10)	−0.13(12)	−0.13(12)	0
	'$4s$'	−0.21(6)	−0.14(7)	−0.14(7)	−0.12(6)
	$r(3d)$	1.10(4)	1.06(4)	1.06(4)	1.04(3)
N(1)	$2p_z$	0	−0.011(9)	−0.014	−0.014
N(2)	$2p_z$	0	0.006(11)	0.005(11)	0.003(10)
N(3)	$2p_z$	0	−0.018(8)	−0.014	−0.014
N(4)	$2p_z$	0	−0.012(10)	−0.014(5)	−0.014(5)
C(1)	$2p_z$	0	−0.020(10)	−0.016(6)	−0.015(6)
C(8)	$2p_z$	0	−0.008(10)	−0.010(10)	−0.009(10)
C(9)	$2p_z$	0	0.019(11)	0.018(10)	0.018(10)
C(16)	$2p_z$	0	−0.016(11)	−0.016	−0.015
R		0.272	0.268	0.268	0.268
R'		0.127	0.123	0.123	0.123
χ^2		1.680	1.596	1.584	1.581
No. of variables		6	14	11	9
$F(000)_c$ (B.M. cell^{-1})		1.213	1.106	1.108	1.108

* Footnotes to Table 1 apply here also .

TABLE 3

Orbital spin populations and agreement factors for spin-density distribution models of the [Co(pc)] molecule, based on 482 data[a]

Centre	Variable	Model 1	Model 2	Model 3	Model 4
Co	$3d_{xy}$	0.34(8)	0.40(10)	0.40(10)	0.31(5)
	$3d_{xz}$, $3d_{yz}$	0.22(8)	0.17(10)	0.17(10)	0
	$3d_{z^2}$	0.66(9)	0.79(12)	0.79(12)	0.99(4)
	$3d_{x^2-y^2}$	−0.16(9)	−0.21(10)	−0.21(10)	0
	' 4*s* '	−0.27(5)	−0.14(6)	−0.14(6)	−0.12(5)
	$r(3d)$	1.14(4)	1.07(4)	1.07(4)	1.04(3)
N(1)	$2p_z$	0	−0.02(1)	−0.020	−0.020
N(2)	$2p_z$	0	0.00(1)	−0.004(10)	−0.005(10)
N(3)	$2p_z$	0	−0.02(1)	−0.020	−0.020
N(4)	$2p_z$	0	−0.02(1)	−0.020(5)	−0.020(4)
C(1)	$2p_z$	0	−0.02(1)	−0.017(5)	−0.017(5)
C(8)	$2p_z$	0	−0.01(1)	−0.008(9)	−0.007(9)
C(9)	$2p_z$	0	0.02(1)	0.019(9)	0.020(9)
C(16)	$2p_z$	0	−0.01(1)	−0.017	−0.017
R		0.274	0.269	0.269	0.269
R'		0.137	0.130	0.130	0.130
χ^2		1.723	1.574	1.565	1.573
No. of variables[b]		7	15	12	10
$F(000)_c$ (B.M. cell^{-1})		1.202	1.062	1.062	1.062
Scale, k[b]		0.311(5)	0.310(5)	0.310(5)	0.310(5)

[a] Footnotes to Table 1 apply here also. [b] The number of variables includes a scale factor, k, which is refined in the least-squares process. This scale factor places the 4.6 T F_M data on the same scale as the 1.49 T F_M data. The value of $F(000)$ quoted is the 4.6 T value; $F(000)$ at 1.49 T is obtained by multiplying the 4.6 T value by k.

determined to be very significantly different from zero in the refinements.

As well as those refinements presented in the Tables, several others were attempted using the 337 4.6 T data. The refinement of Model 3, Table 2 was repeated with the constraint, that the cobalt $3d_{xz}$ and $3d_{yz}$ populations be equal, removed. The refinement (12 variables) converged with $3d_{xz}^{0.10(12)}$, $3d_{yz}^{0.14(12)}$, and χ^2 1.587. All other parameters refined to identical values to those quoted in Table 2 (Model 3). This result indicates that the assumption of essential D_{4h} symmetry for the [Co(pc)] molecule is substantiated.

The refinement of Model 3, Table 2 was also repeated using spherically symmetric 2*s* orbitals, rather than $2p_z$ orbitals, centred on each of the inner-ring ligand N and C atoms. The refinement (11 variables) converged with χ^2 slightly greater (1.603), and all populations essentially unchanged. As expected, the data do not define well the angular variation of the spin densities on the ligand atoms, although the model with ligand density of $2p_z$ angular dependence was slightly preferred.

In order to check the effects of extinction on the 4.6 T data, a refinement was performed employing an extinction correction of the type previously described.[8] The extinction parameter refined to a value less than one standard deviation from zero. A refinement was also performed with the 80 reflections with the largest F_N values rejected. These rejected data would show the largest effects of any extinction present. This refinement (9 variables including only 3 ligand populations, 257 observations) converged with χ^2 1.415. The Co spin populations were $3d_{xy}^{0.28(12)}$, $d_{xz,yz}^{0.20(12)}$, $d_{z^2}^{0.60(14)}$, $d_{x^2-y^2}^{-0.16(13)}$, ' 4*s* '$^{-0.07(7)}$. These results indicate the essential absence of extinction effects.

From the refinements presented in Tables 1—3, values of $F(000)$ are obtained by extrapolation of the molecular magnetic form factor to $(\sin\theta)/\lambda = 0.0$. Although we cannot give proper estimates of the errors in the $F(000)$ values quoted, the 4.6 T value is quite accurately determined by the experiment. This is because the low $(\sin\theta)/\lambda$ data are the most accurate, and extend to relatively low $(\sin\theta)/\lambda$ values because of the large unit cell, and because the model includes the ligand forward peak in the form factor. The $F(000)$ value at 4.6 T is 1.09 B.M. cell^{-1} (Tables 2 and 3). This is the value of the magnetic moment $\langle\mu_b\rangle$ at this magnetic field. The 1.49 T $F(000)$ value is less well defined, due to the lower precision of the data, and is determined as either 0.26 or 0.33 B.M. cell^{-1} (Tables 1 and 3).

Observed and calculated (Model 3, Table 3) magnetic structure factors (B.M. unit cell^{-1}) are listed in Supplementary Publication No. SUP 22934 (8 pp.).* Data reduction (flipping ratios to F_M values) and statistical analyses were performed using the University of Western Australia computer programs.[16] All computations were performed on a CDC CYBER 73 computer at the Western Australian Regional Computing Centre.

DISCUSSION

The best-defined feature of our results is the set of *d*-orbital spin populations on the cobalt atom. The errors listed in Tables 1—3 for the values of these populations are those given by the least-squares fitting program and, unfortunately, are almost certainly underestimates of the true uncertainties. In our analysis of the p.n.d. data for $Cs_3[CoCl_4]Cl$, we deduced[8] that systematic effects such as extinction, multiple scattering, and uncertainty in the description of the ground state and in the applicability of the dipole approximation correction[21] for the orbital scattering could increase the error in the individual *d*-orbital spin populations to about 0.1 electron in the $CoCl_4^{2-}$ ion. On account of both the lower magnetisation available in the present compound, because of the lower spin of the system ($S = \frac{1}{2}$ against $S = \frac{3}{2}$ in $Cs_3[CoCl_4]Cl$), and the large size of a complete data set, which we could not hope to measure, the present data are significantly less accurate and less extensive than those for $Cs_3[CoCl_4]Cl$. The correction for orbital scattering is also greater ($g_b = 2.5$ *versus* $\bar{g} = 2.4$), and as [Co(pc)] departs more from spherical symmetry the basis for the spherical dipole approximation[21] used for this correction is less certain. Consequently, it is likely that the errors in the *d*-orbital populations in [Co(pc)] are larger than those in $Cs_3[CoCl_4]Cl$. The discussion of the *d*-orbital spin populations in [Co(pc)] must proceed, therefore, with an uncertainty of more than 0.1 electron in each individual member in mind. The best determination of the model parameters is from the refinement employing all 482 observations, and with as many constraints on the ligand orbital populations as is reasonable (Model 3, Table 3). These spin population values will be used in the following discussion.

The Cobalt Electronic Structure.—The negative spin in the $d_{x^2-y^2}$ orbital, and also that apparently in the ' 4*s* ' orbital and on the ligand macrocycle, can only arise through spin polarisation effects. Spin polarisation arises because the presence of, say, up-spin tends to increase the amount of up-spin in its own vicinity, and

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

consequently to create down-spin elsewhere. It occurs as a result of interelectron correlation, and so is very difficult to quantify in a system as large as a transition-metal ion. Some further discussions of its implications will take place below, but for the present purposes we may merely note that the origin of the negative spin is different from that of the major positive spin populations.

For the cobalt atom our model is the minimal orbital basis set 3*d*–4*s* and the positive *d* spin populations may be regarded as ' holes ' in a filled d^{10} shell, and one may proceed from them to the *d*-electron population set ${d_{xy}}^{1.60}$, ${d_{xz}}^{1.83}$, ${d_{yz}}^{1.83}$, ${d_{z^2}}^{1.21}$. The negative $d_{x^2-y^2}$ spin population may be treated as an electron population, giving a total cobalt *d* population ${d_{xy}}^{1.60}$, ${d_{xz}}^{1.83}$, ${d_{yz}}^{1.83}$, ${d_{z^2}}^{1.21}$, ${d_{x^2-y^2}}^{0.21} \equiv 3d^{6.68}$, which is to be compared with that for a formal Co^{2+} ion of $3d^7$. The meaning of the negative spin apparently in the ' 4*s* ' orbital is less certain. It could be an electron population resulting from polarisation of spin transferred into an empty 4*s* orbital, giving ' 4*s* ' $^{0.14}$, or from the polarisation of a filled ' 4*s* ' orbital, giving the electron population ' 4*s* ' $^{1.86}$. Our experiment cannot differentiate between these possibilities. The former leads to a cobalt atom with a formal charge of $(9 - 6.68 - 0.14) = 2.18$, the latter to one of $(9 - 6.68 - 1.86) = 0.46$. On the grounds of the apparently obvious covalence of bonding in the metallophthalocyanines, perhaps the figure of *ca.* 0.5 is the more acceptable, and this figure is supported by our estimate, based upon *X*-ray diffraction measurements, that in the entirely similar manganese analogue, [Mn(pc)], the 4*s*-like orbital is filled.[17] However, an *ab-initio* calculation on porphyrinatocobalt(II) does not support much covalency involving the metal *d* orbitals, and indicates a residual charge of *ca.* 1.8 on the cobalt atom.[23]

Comparison with E.S.R. Results.—The e.s.r. parameters for square-planar cobalt(II) complexes place severe restrictions on the ground-state *d*-orbital populations from which they arise. It is generally accepted that the $d_{x^2-y^2}$ orbital, directed at the nitrogen ligand donor atoms, lies so high in energy that it plays no part in the electronic structure of the ground levels. The investigation of the doublet terms which arise from the configuration $(d_{xy}d_{xz}d_{yz}d_{z^2})^7$ is relatively straightforward. The *g* values and the hyperfine tensor components arising from the various ground terms have been given [3] as a function of the eigenvector coefficients resulting from the solution of the matrix (below) where the superscripts +

$$\begin{array}{cccc} {d_{yz}}^+ & {d_{xz}}^+ & {d_{z^2}}^- & {d_{xy}}^- \\ \Delta_{yz} & i\lambda/2 & i\lambda 3^{\frac{1}{2}}/2 & -\lambda/2 \\ -i\lambda/2 & \Delta_{xz} & \lambda 3^{\frac{1}{2}}/2 & i\lambda/2 \\ -i\lambda 3^{\frac{1}{2}}/2 & \lambda 3^{\frac{1}{2}}/2 & \Delta_{zz} & 0 \\ -\lambda/2 & i\lambda/2 & 0 & 0 \end{array}$$

and − refer to spin quantum numbers $m_s = \pm\frac{1}{2}$. The diagonal elements of this matrix are the separations between the *d* orbitals under consideration, in the absence of spin–orbit coupling, and include not only ligand-field terms but also interelectronic repulsion effects. The energy of the d_{xy} orbital is defined as zero. The diagonal elements may be expected to be reproduced by a ligand-field model in conjunction with reasonable interelectronic repulsion parameters for the Co^{2+} ion. In the case of the d^7 configuration, the matrix describes ' holes ' in the filled d^{10} shell, and the ligand-field and spin–orbit coupling parameters to be employed in the actual calculation are reversed in sign.

It is quickly established firstly that, unless the d_{xy} orbital lies lowest in energy, it is not relevant to the determination of the e.s.r. parameters, and secondly that if one of the d_{xz}, d_{yz}, and d_{z^2} orbitals lies lowest, then these orbitals must lie with a separation which is not very much greater than ζ_{3d}. This treatment ignores the possible mixing of the d_{z^2} orbital with the 4*s* orbital, which has the same symmetry (a_{1g} in D_{4h}, a_1 in C_{2v}) and is believed to lower its energy. Participation by the 4*s* orbital would affect the calculation of the *g* values, but probably not g_z by a great deal since it has the same value of m_l, 0, as the d_{z^2} orbital.

Taking the value of ζ_{3d} for the Co^{2+} ion in [Co(pc)] as 450 cm^{-1}, the particular pattern of the *g* values for [Co(pc)], $g_z = 1.91$, $g_x = 2.92$, $g_y = 2.89$,[22] unambiguously requires the d_{z^2} orbital to lie lowest with d_{xz} and d_{yz} degenerate to within *ca.* 100 cm^{-1}, lying between about 1 000 and 3 000 cm^{-1} higher. It is not possible to fix the d_{z^2}–d_{xz}, d_{yz} separation closely since the expressions for the *g* values involve the orbital reduction parameter, *k*, and this cannot be established from the e.s.r. data alone. A value of *k* of 0.8, however, must be considered very reasonable in such a compound as [Co(pc)] and this is consistent with a d_{z^2}–d_{xz},d_{yz} separation of *ca.* 2 000 cm^{-1}. The ratio of that separation to ζ_{3d} is sufficiently large (*ca.* 4.5) that the ground state may be considered to be orbitally non-degenerate and the use of the dipole correction for orbital scattering of the polarised neutrons is justified at least to a first approximation. This ratio fixes the eigenvector coefficients of the matrix above, and hence the corresponding *d*-orbital populations, giving the configuration ${d_{xy}}^{1.98}$,${d_{xz}}^{1.93}$,${d_{yz}}^{1.93}$,${d_{z^2}}^{1.16}$.

The results of our p.n.d. experiment are in concordance with the deductions [3] from the e.s.r. data in some, but not all, features. The amount of population of the d_{z^2} orbital is in agreement, and that is probably the most important point to be looked for. Also, the d_{xz} and d_{yz} populations are equal and differ from 2.0 only by a relatively small, but non-zero, amount. The disagreement lies in the d_{xy} population: in the analysis of the e.s.r. data it is clear that this orbital should be completely filled, while the p.n.d. experiment finds a substantial (0.4 e) vacancy in it. The analysis of the e.s.r. data ignores the quartet terms of the d^7 configuration, as it has been pointed out that they are indeed not likely to be directly important.[24] However, there remains the possibility that, in the presence of fairly large spin–orbit coupling, quartet–doublet mixing could be a factor in the ground-state composition if certain quartet terms lie sufficiently near the ground doublet term. We performed a series of calculations of the ground-state *g* values and *d*-orbital populations arising from the entire d^3 manifold in the presence of a ligand-field perturbation, interelectronic repulsions, and spin–orbit coupling, diagonalising one of the two resultant equivalent matrices of order 60. The ligand-field perturbation was introduced in the form of angular-overlap model parameters, changing values somewhat from those used for square-planar cobalt(II) Schiff-base compounds so as to raise the d_{z^2} orbital and force the ground term to be $^2A_1$ with the unpaired electron in the d_{z^2} orbital, rather than $^2A_2$ with it in the d_{yz} orbital. The values of the parameters employed for the ligand nitrogen atoms were $e_\sigma = 12\,000$, $e_{\pi\perp} = 4\,300$, $e_{\pi\|} = 7\,000$ cm^{-1} [9 200, 2 800, and 4 600 cm^{-1} respectively were used[4] for *NN'*-ethylenebis(salicylideneiminato)cobalt(II)] but the choice is not unique. It was found that the predictions were but little different from those of the simpler theory using the matrix above, provided the d_{z^2}–d_{xz}, d_{yz} separation was arranged to be the same. No d_{xy} population less than 1.98 was deduced, nor any $d_{x^2-y^2}$ population.

Spin Polarisation Effects.—Direct spin polarisation of one orbital by another takes place only if they are of the same symmetry, as it can be regarded as a form of configurational interaction. Indirect spin polarisation *via* the core electrons relaxes this requirement, but is expected to be rather small. It is possible, then, that the negative spin in the $d_{x^2-y^2}$ orbital and in the ' 4s ' orbital is the result of spin polarisation by the d_{z^2} orbital, as all have the same symmetry, A_1, in the group C_{2v}. However, the fact that the cobalt atom site symmetry in [Co(pc)] approximates quite closely to D_{4h} (confirmed by the near degeneracy of the d_{xz} and d_{yz} orbitals which is implied by the near equality of g_x and g_y) reduces the force of this argument in relation to the $d_{x^2-y^2}$ population.

The Ligand Spin Populations.—The ligand spin populations have been assigned to p_π orbitals, since there is no evidence from ^{1}H n.m.r. contact shift studies on cobalt(II) porphyrins for spin in the σ ligand orbitals.[25, 26] In practice, the scattering of the polarised neutrons from a p orbital differs only in detail according to the orientation and is very similar from an s orbital of the same radial extent, so our analysis really does not distinguish between π and σ spin density on the macrocycle atoms. Our analysis of the ligand spin populations has been necessarily restricted because the limited amount and quality of data available does not support the large number of parameters that would be required for a full treatment. We have ignored the possibility of spin in the benzene ring sections of the molecule, although the ^{1}H n.m.r. contact shift results on cobalt(II) porphyrins[26] indicate that values on the ' pyrrole ' carbon atoms {equivalent to C(2), C(7), C(10) and C(15) of the [Co(pc)] structure} are not much lower than on the ' *meso* ' carbon atoms {which correspond to the aza-bridges, N(1) and N(3), of [Co(pc)]}. We have also constrained some of the populations to be equal by arguments of approximate symmetry, supported by similar values obtained on separate refinement, in order to keep the number of variable parameters to a minimum.

The least-squares derived errors on the p-orbital populations quoted in Tables 1—3 are again undoubtedly underestimates, and since the populations involved are only a few times the least-squares error values, our discussion of the results must be limited to some general largely qualitative observations.

Unfortunately, direct comparison of our deductions with the ^{1}H n.m.r. contact shift results is not possible since the same atoms are not involved. The nearest equivalence available is between the *meso* carbon atom of the porphyrins and the aza-bridge nitrogen atom in [Co(pc)]. However, the contact shifts[26] for all the protons in the cobalt(II) porphyrins are quite small (<4 p.p.m. at 35 °C) and spin populations all around the porphyrin macrocycle are deduced to be small, say less than 1×10^{-3} unpaired electron on any atom using formulae from ref. 27. This result was seen to be in accord with the belief that the d_{xz} and d_{yz} orbitals were filled, so that d_π–p_π overlap between the cobalt atom and the macrocycle is absent. Our results, then, are in some conflict with the ^{1}H n.m.r. contact shift interpretations, for the similarity of the e.s.r. g values shows the close analogy between the electronic structures of [Co(pc)] and the cobalt(II) porphyrins. It is also to be noted that the alternation in the spin on atoms in π systems, characteristic of ^{1}H n.m.r. contact shift data analyses, is probably absent in our results. Given the negative spin on N(2) and N(4), on that basis one would have expected positive spin on C(1), C(8), C(9), and C(16); in fact, the spin on all these atoms is negative or zero within the least-squares errors. Our spin populations are not of sufficient accuracy to make worthwhile their comparison with, say, the coefficients of the Hückel-type molecular-orbital calculations such as have been developed to account for the contact shift results for iron(II) high-spin porphyrins.

Although the individual macrocycle-atom spin populations derived from our data are subject to quite some uncertainty, there is no doubt that the overall spin density on the ligand is negative. If the magnetisation along the b crystal axis at 4.6 T were available, a direct confirmation of this would follow, as the cobalt atom d-orbital populations would then be on an absolute scale. The sum of the macrocycle atom spin populations is −0.17(5) electrons, and the error in this value is a good deal less than the sum of the errors in the individual populations. We can say with some confidence that there is transfer of about 15% of the spin of the central cobalt atom to the ligand, albeit not through simple covalent overlap interactions (which would lead to positive spin on the ligand) but through spin polarisation effects, as no treatment which does not distinguish between up-spin and down-spin can introduce negative spin densities. In support of this argument, the *ab-initio* calculation performed upon porphyrinatocobalt(II) has indicated that covalent mixing of the metal d orbitals with the ligand orbitals is quite small.[23]

The polarisation transfer of spin to the ligand is usually presumed to take place through a charge-transfer mechanism. In the metal porphyrin compounds[25] charge transfer from a filled ligand π molecular orbital to the $d_{\pi_\parallel}$ (d_{xz},d_{yz}) orbitals is assumed. The interaction of the $d_{\pi_\perp}$ orbital (d_{xy}) is neglected, although the angular-overlap model parameter, e_π, associated with it is not much smaller than that concerning the $d_{\pi_\perp}$ orbitals, $e_{\pi_\perp}$. If the metal d_π orbitals are empty, positive spin is taken to be preferred on the metal atom to ensure the greatest number of unpaired electrons possible, and negative spin is left on the ligand. If the metal d_π orbitals are half-filled or more, the metal atom must accept negative spin, resulting in positive spin on the ligand. For cobalt(II) porphyrin compounds the d_π orbitals are taken to be filled, and this mechanism is not available.[25,26] If the filling is not quite complete, as we propose for [Co(pc)] and by inference for the cobalt(II) porphyrins, the result at most would be the transfer of a small amount of positive spin to the macrocycle.

It seems then that the transfer of negative spin to the ligand macrocycle in [Co(pc)] may proceed through the σ-bonding framework, rather than through the π system. The most likely mechanism is probably associated also with the polarisation of the '4*s*' orbital. Assuming [Co(pc)] belongs to the point group D_{4h}, one of the bonding molecular orbitals of the complex is of A_{1g} symmetry and this presumably has as its major metal-based component the 4*s* orbital. However, the d_{z^2} orbital also is of A_{1g} symmetry, and this contains most of the spin of the system. Spin polarisation can be considered to take the form that the $d_{z^2}{}^-$ orbital radial function is of more diffuse extent, seeking to avoid sharing space in common with the dominant spin component $d_{z^2}{}^+$, of more contracted radial extent. This more diffuse $d_{z^2}{}^-$ orbital shares more space in common with the 4*s* orbital and with the ligand donor atom p_σ orbitals, and so it introduces negative spin onto the ligand. Unfortunately, it does not seem possible to make this argument more quantitative in a molecule as large as [Co(pc)].

The Magnetic Properties.—There are two molecules in the unit cell of [Co(pc)], so the value of $F(000)$ of 1.09 B.M. at 4.6 T leads to $\langle\mu_b\rangle = 0.545$ B.M. per molecule, and this, in conventional usage, is assigned to the cobalt atom. The magnetisation of the polycrystalline material at 4.6 T and 4.2 K corresponds to $\langle\bar{\mu}\rangle = \chi_m H/N\beta = 0.70$ B.M.[11] In order to compare these results it is necessary to take account of the magnetic saturation. At 4.6 T and with $g_b = 2.50$ the value of $\langle\mu_b\rangle$ expected for an $S = \frac{1}{2}$ system in the absence of magnetic exchange is $\langle\mu_b\rangle_0 = \frac{1}{2}g_b B(\frac{1}{2}, \mathrm{a}) = 0.83$ B.M., where $B(\frac{1}{2}, \mathrm{a})$ is the Brillouin function for $J = \frac{1}{2}$, and $\mathrm{a} = \frac{1}{2}g_b\beta H/4.2k$. From the p.n.d. experiment, then, $\langle\mu_b\rangle/\langle\mu_b\rangle_0 = 0.66$.

At 4.6 T, with $\bar{g} = 2.61$, at 4.2 K $\langle\bar{\mu}\rangle_0 = \frac{1}{2}\bar{g}B(\frac{1}{2}, \mathrm{a}) = 0.93$ B.M., with $\mathrm{a} = \frac{1}{2}\bar{g}\beta H/4.2k$. From the magnetisation measurement, $\langle\bar{\mu}\rangle/\langle\bar{\mu}\rangle_0 = 0.75$. The similarity of this to the ratio for the p.n.d. experiment indicates that the effect of the magnetic exchange along the *b* axis is little different to that for the powder. That result also holds in [Mn(pc)].[28]

In [Mn(pc)], $\theta_\parallel$, corresponding to the Curie–Weiss law for the magnetic susceptibility parallel to the pseudo-C_4 axis of each molecule, is much smaller than $\theta_\perp$, which is associated with the susceptibility perpendicular to that C_4 axis. The value of θ_b is found to be very close to $\bar{\theta}$, as the C_4 axis lies close to 45° to the *b* axis.

Conclusions.—The p.n.d. experiment on a molecule as large as [Co(pc)] and with spin of only $S = \frac{1}{2}$ yields information of considerable chemical interest. The *d*-orbital populations are defined with worthwhile accuracy, and there is evidence of spin transfer by polarisation effects into a diffuse cobalt-centred orbital ('4*s*') and onto the ligand macrocycle. Relative to the results on smaller molecules of higher spin quantum number ($CrF_6{}^{3-}$ and $CoCl_4{}^{2-}$ ions), the information is, as expected, less precise, and in some aspects it is only semi-quantitative in nature. It is not possible, for instance, to clearly define the spin on each of the atoms of the ligand macrocycle nor to observe spin density in the metal–donor atom overlap region. Anisotropy of the spin delocalised onto the ligand donor atoms, consequent upon the difference between σ and π bonding, was not observed. All of the above features were apparent, for example, in the studies of the $CrF_6{}^{3-}$ and $CoCl_4{}^{2-}$ ions.[7,8]

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