Structure of Phthalocyaninatocobalt(II) at 4.3 K: A Neutron-diffraction Study

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The crystal and molecular structure of the β-polymorphic form of phthalocyaninatocobalt(II), [Co(pc)], has been determined by single-crystal neutron-diffraction methods at 4.3 K. Crystals are monoclinic, space group $P2_1/c$, with a = 14.495(5), b = 4.742(4), c = 19.107(5) Å, β = 120.76(2)°, and Z = 2. Automatic diffractometry has provided Bragg intensities for 1 261 independent reflections. Data are of limited resolution along the b axis direction (hkl with $k \leqslant 2$). The structure has been refined by full-matrix least-squares methods to R 0.031. Bond lengths at 4.3 K show systematic deviations from those determined at 295 K by X-ray diffraction data of moderate resolution. This is explained primarily in terms of errors in the X-ray determined atomic positions due to the effects of asphericity of the valence electrons, with thermal motion at 295 K having only a small effect. Within the central cavity of the macrocyclic phthalocyaninate ligand, the cobalt atom co-ordinates to a precisely planar array of nitrogen atoms, with Co–N bond lengths 1.908(2) and 1.915(2) Å at 4.3 K which differ significantly from the values obtained at 295 K by X-ray diffraction. The neutron-scattering length of cobalt has been found by least-squares refinement to be 0.252(7) × 10^{-12} cm.

METALLOPHTHALOCYANINES have been studied extensively by single-crystal X-ray diffraction techniques at temperatures of 116 and 300 K (ref. 1 and references therein). The β-polymorphic form of phthalocyaninatocobalt(II), [Co(pc)] (Co^{II}, $S = \frac{1}{2}$), remains a paramagnet at 4.2 K,[2] whereas β-phthalocyaninatomanganese(II), [Mn(pc)] (Mn^{II}, $S = \frac{3}{2}$), is a rare example of a ferromagnetic molecular crystal, with T_c = 8.6 K.[3,4] These two compounds have been chosen for initial studies in a wide-ranging programme aimed at determining the spin-density distributions in paramagnetic crystals using the technique of polarised neutron diffraction.[5]

The crystal and molecular structure of the β-polymorphic form of [Co(pc)] has been determined at 295 K by single-crystal X-ray diffraction methods,[1] and a determination of the structure at 4.3 K by single-crystal neutron-diffraction methods is reported below. These studies have been undertaken to assist both in the treatment of the 4.2 K polarised neutron data and in the interpretation of the ensuing spin-density distribution in [Co(pc)].[6]

EXPERIMENTAL

Large single crystals of [Co(pc)] suitable for neutron-diffraction studies were grown, with difficulty, by entrainer vacuum sublimation under conditions already described.[7] Crystal data for both the present study and the 295 K X-ray diffraction study are presented in Table 1. Neutron-diffraction intensity data were obtained at 4.3 K on the D15 normal-beam diffractometer with motorised lifting counter, located at a thermal-neutron inclined beam of the Institut Laue-Langevin high-flux reactor. The (331) reflection of a Cu crystal monochromator in transmission was used, with a take-off angle θ_M of 45°, to produce a beam with λ 1.175 Å and a flux of 8.1 × 10^6 n cm^{-2} s^{-1}. The λ/2 contamination was <0.08%. The crystal was mounted on the diffractometer with its rotation axis offset by *ca.* 5° from the crystallographic b axis (needle axis) in order to minimise multiple diffraction effects. The space group was verified as $P2_1/c$ by confirming the systematic absences $0k0$ for k odd and $h0l$ for l odd, on the diffractometer. Unit-cell parameters, together with their estimated standard deviations (e.s.d.s), were derived by a least-squares analysis of the setting angles determined for 10 angularly well separated reflections. The temperature was monitored throughout the data collection and remained steady at 4.3 ± 0.1 K. Intensities were measured *via* an ω—2θ scan, and no significant variation in the intensity of a standard reflection was observed throughout the data collection. Integrated intensities were obtained using a profile-analysis program, COLL5,[8] and geometrical corrections were applied. Absorption corrections were not considered necessary due to the small linear absorption coefficient (Table 1).

TABLE 1

Crystal data for [Co(pc)], $C_{32}H_{16}CoN_8$; M = 571.48, space group $P2_1/c$, Z = 2

	295 K	4.3 K
a/Å	14.542(2)	14.495(5)
b/Å	4.773 1(5)	4.742(4)
c/Å	19.352(2)	19.107(5)
β/°	120.824(7)	120.76(2)
U/Å^3	1 153.49	1 128.56
D_c/g cm^{-3}	1.645	1.681
λ/Å	0.709 26 (X-Ray)	1.175 (Neutron)
μ/cm^{-1} [a]	8.214	0.061
Crystal dimensions/mm [b]	0.10 × 0.16 × 0.26	1.0 × 1.5 × 10.6
Unique data	1 930 [$I > 3\sigma(I)$]	1 261 [c]
Limit (Å^{-1}) of (sinθ)/λ	0.705	0.736
No. of variables	219	156
R	0.039	0.031
R'	0.040	0.026

[a] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1968, vol. 3, pp. 162, 197. [b] The largest dimension in each case coincides with the b axial direction. [c] All observed data.

The cryostat design on the D15 diffractometer prevented the lifting detector being raised more than 30° above the equatorial plane. Therefore, only the $h0l$, $h1l$, and a very small portion of the $h2l$ data were accessible; consequently, atomic parameters associated with the b crystallographic direction are less precise than other parameters. All data that could be obtained within the above hardware limit, and within the limit $(\sin\theta)/\lambda \leqslant 0.74$ Å^{-1}, were measured, and in most cases it was possible to scan two equivalent reflections. The intensities of these equivalent observations, in good agreement in all cases, were averaged. Of the 1 261 unique reflections observed and used in the refinement, 406, 784, and 71 were in the $h0l$, $h1l$, and $h2l$ layers respectively.

Structure Refinement.—The structure was refined using the least-squares program CRYLSQ [9] in the full-matrix mode, the function minimised being $\Sigma w(\Delta F)^2$ where w is the weight, based on counting statistics, assigned to the $|F_o|$ values, and $\Delta F = |F_o| - |F_c|$. All 1 261 observations, none of which had a negative intensity, were used in the refinement.

TABLE 2

Final atomic positional and thermal parameters for [Co(pc)] at 4.3 K.† Anisotropic and isotropic thermal parameters are defined by $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$ and $T = \exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$

Atom	x/a	y/b	z/c	$10^3U/$ Å^2
Co	0	0	0	2.5(1.3)
N(1)	0.253 5(1)	0.027 0(7)	0.161 7(1)	3.8(2)
N(2)	0.073 5(1)	0.217 8(7)	0.097 5(1)	3.4(2)
N(3)	−0.071 1(1)	0.526 9(7)	0.078 8(1)	3.9(2)
N(4)	−0.131 3(1)	0.197 2(7)	−0.033 1(1)	3.3(2)
C(1)	0.179 7(1)	0.194 8(10)	0.158 8(1)	3.1(2)
C(2)	0.202 5(1)	0.396 7(10)	0.223 3(1)	3.0(2)
C(3)	0.294 7(1)	0.451 3(11)	0.298 1(1)	4.3(2)
C(4)	0.287 1(1)	0.661 6(11)	0.346 4(1)	4.4(2)
C(5)	0.190 9(1)	0.808 8(10)	0.320 9(1)	4.5(3)
C(6)	0.099 2(1)	0.753 7(10)	0.246 1(1)	4.2(2)
C(7)	0.107 1(1)	0.544 8(10)	0.198 2(1)	3.0(2)
C(8)	0.028 5(1)	0.431 3(10)	0.119 4(1)	3.2(2)
C(9)	−0.144 4(1)	0.413 0(10)	0.009 3(1)	2.9(2)
C(10)	−0.255 3(1)	0.502 4(10)	−0.032 7(1)	3.1(2)
C(11)	−0.307 9(1)	0.705 3(10)	−0.013 2(1)	4.2(2)
C(12)	−0.417 8(1)	0.738 0(10)	−0.066 8(1)	5.0(3)
C(13)	−0.473 1(1)	0.570 8(10)	−0.137 6(1)	4.8(2)
C(14)	−0.419 7(1)	0.369 6(10)	−0.156 6(1)	4.1(2)
C(15)	−0.309 6(1)	0.338 4(10)	−0.102 9(1)	3.0(2)
C(16)	−0.230 0(1)	0.154 2(10)	−0.102 3(1)	2.9(2)
H(1)	0.369 1(2)	0.342 7(23)	0.317 5(2)	
H(2)	0.356 7(2)	0.713 1(22)	0.405 5(2)	
H(3)	0.187 8(2)	0.960 9(24)	0.360 0(2)	
H(4)	0.024 3(2)	0.863 6(24)	0.225 6(2)	
H(5)	−0.264 7(2)	0.832 4(23)	0.041 1(2)	
H(6)	−0.461 8(2)	0.891 0(24)	−0.054 1(2)	
H(7)	−0.559 1(2)	0.605 3(22)	−0.178 6(2)	
H(8)	−0.462 4(2)	0.243 8(22)	−0.211 2(2)	

	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
H(1)	12(1)	24(16)	20(1)	6(3)	5(1)	−2(3)
H(2)	13(1)	11(15)	12(1)	1(3)	0(1)	−6(3)
H(3)	21(1)	46(16)	15(1)	0(3)	9(1)	−9(3)
H(4)	12(1)	54(17)	20(1)	7(3)	6(1)	−2(3)
H(5)	17(1)	20(16)	15(1)	3(3)	5(1)	−10(3)
H(6)	16(1)	32(17)	22(1)	6(3)	8(1)	−5(3)
H(7)	7(1)	40(17)	17(1)	8(3)	1(1)	1(3)
H(8)	17(1)	13(16)	14(1)	2(3)	4(1)	−5(3)

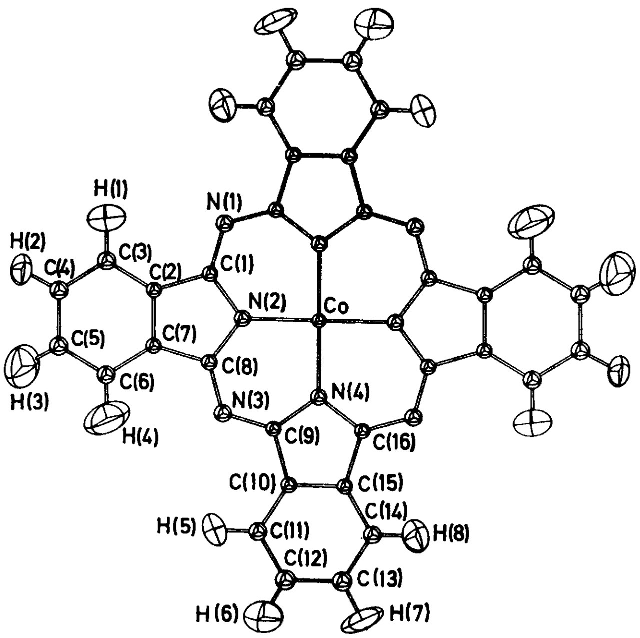
† The e.s.d.s (in parentheses) are those obtained in the usual manner from the least-squares refinement.

Starting parameters were obtained from the 295 K structure of [Co(pc)],[1] with the exception of H atoms which were initially placed in idealised positions. After several cycles of refinement an examination of observed and calculated structure factors indicated the presence of significant secondary extinction effects. Further refinement included an isotropic extinction correction,[9] together with positional and thermal (Co,N,C isotropic; H anisotropic) parameters, and the scattering length of cobalt (156 variables). Refinement converged with R $(=\Sigma|\Delta F|/\Sigma|F_o|)$ 0.031 and R' $\{=[\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ 0.026. The maximum parameter shift-to-error ratio at convergence was 0.12 : 1. A final difference synthesis was essentially featureless, the maximum and minimum densities being 0.057 and -0.057×10^{-12} cm Å^{-3}. The extinction coefficient was refined to $5.79(6) \times 10^3$, assuming an average transmission path length of 1.2 mm. The neutron-scattering length of cobalt refined to $0.252(7) \times 10^{-12}$ cm, with the scattering lengths for C, H, and N taken from ref. 10.

Final atomic positional and thermal parameters are listed in Table 2. Observed and calculated structure factors and details of least-squares planes are listed in Supplementary Publication No. SUP 22789 (9 pp.).* All computations were performed on a DEC-10 computer at the Institut Laue-Langevin.

DISCUSSION

The molecular geometry at 4.3 K and atom numbering of the centrosymmetric [Co(pc)] molecule are shown in the Figure. Interatomic distances, angles, and correlated e.s.d.s † are given in Tables 3 and 4, together with the corresponding values obtained from the 295 K X-ray diffraction study for comparison.[1] The 295 K bond distances, corrected for thermal motion, are also presented in Table 3. For this correction for apparent bond shortening due to thermal vibrations, the rigid-body TSL method of Schomaker and Trueblood [11] was



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

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

† The e.s.d.s contain contributions from the e.s.d.s in the cell parameters.

applied to three segments of the molecule, and each was treated as an isolated rigid body. The first segment contained the 16 inner-ring atoms together with the cobalt atom, while the second and third segments comprised the eight carbon atoms C(1)—C(8) and C(9)—C(16). No more sophisticated modelling of the molecular thermal motion was appropriate in this case, due to almost certain bias in the 295 K thermal parameters introduced by the limited resolution of the data.

TABLE 3

Interatomic distances (Å) in [Co(pc)]

(*a*) Intramolecular distances[a]

	295 K	295 K[b]	4.3 K
Co–N(2)	1.906(2)	1.907(2)	1.908(2)
Co–N(4)	1.909(2)	1.911(2)	1.915(2)
N(1)–C(1)	1.318(4)	1.319(4)	1.312(4)
N(1)–C(16′)	1.313(4)	1.314(4)	1.321(4)
N(2)–C(1)	1.385(3)	1.386(3)	1.382(1)
N(2)–C(8)	1.368(4)	1.369(4)	1.380(5)
N(3)–C(8)	1.318(4)	1.318(4)	1.321(2)
N(3)–C(9)	1.318(3)	1.319(3)	1.320(3)
N(4)–C(9)	1.369(4)	1.370(4)	1.377(5)
N(4)–C(16)	1.378(3)	1.379(3)	1.379(1)
C(1)–C(2)	1.451(4)	1.454(4)	1.459(5)
C(2)–C(3)	1.386(3)	1.388(3)	1.394(2)
C(2)–C(7)	1.383(4)	1.387(4)	1.400(4)
C(3)–C(4)	1.378(5)	1.380(5)	1.401(5)
C(4)–C(5)	1.386(5)	1.389(5)	1.405(4)
C(5)–C(6)	1.381(4)	1.383(4)	1.391(2)
C(6)–C(7)	1.384(5)	1.387(5)	1.392(5)
C(7)–C(8)	1.448(3)	1.450(3)	1.448(3)
C(9)–C(10)	1.449(4)	1.451(4)	1.446(3)
C(10)–C(11)	1.383(5)	1.385(5)	1.391(5)
C(10)–C(15)	1.385(4)	1.388(4)	1.394(4)
C(11)–C(12)	1.381(4)	1.384(4)	1.394(2)
C(12)–C(13)	1.385(5)	1.388(5)	1.412(4)
C(13)–C(14)	1.379(6)	1.381(6)	1.389(5)
C(14)–C(15)	1.385(4)	1.388(4)	1.395(2)
C(15)–C(16)	1.452(5)	1.454(5)	1.443(4)
H(1)–C(3)	0.92(3)	0.92(3)	1.075(7)
H(2)–C(4)	0.95(3)	0.95(3)	1.089(4)
H(3)–C(5)	0.95(4)	0.95(4)	1.056(9)
H(4)–C(6)	0.97(3)	0.98(3)	1.081(7)
H(5)–C(11)	0.93(3)	0.93(3)	1.081(7)
H(6)–C(12)	0.96(5)	0.96(5)	1.072(9)
H(7)–C(13)	0.96(3)	0.96(3)	1.094(3)
H(8)–C(14)	0.96(3)	0.96(3)	1.080(7)
Co ··· N(1)	3.370(2)	3.372(2)	3.384(2)
Co ··· N(3)	3.336(3)	3.337(3)	3.340(3)
N(2) ··· N(4)	2.714(3)	2.716(3)	2.733(2)
N(2) ··· N(4′)	2.681(4)	2.683(4)	2.672(4)

(*b*) Intermolecular contacts perpendicular to molecular plane[a, c]

	295 K	4.3 K
Co ··· N(3″)	3.219(3)	3.154(3)
Co ··· C(8″)	3.469(3)	3.418(4)
Co ··· C(9″)	3.593(3)	3.541(4)
N(1) ··· C(2″)	3.463(4)	3.429(6)
N(1) ··· C(7″)	3.466(5)	3.426(4)
N(1) ··· C(10‴)	3.379(5)	3.335(4)
N(1) ··· C(15‴)	3.486(4)	3.451(6)
N(2) ··· C(6″)	3.526(4)	3.458(4)
N(2) ··· N(4‴)	3.344(4)	3.312(5)
N(2) ··· C(9‴)	3.276(5)	3.229(4)
N(4) ··· C(8‴)	3.302(5)	3.249(4)
C(1) ··· C(6″)	3.310(5)	3.242(5)
C(1) ··· C(7″)	3.520(5)	3.462(7)
C(1) ··· C(10‴)	3.468(5)	3.432(4)
C(1) ··· C(15‴)	3.437(5)	3.413(5)
C(1) ··· C(16‴)	3.501(4)	3.469(6)
C(2) ··· C(5″)	3.469(5)	3.405(6)
C(2) ··· C(16‴)	3.352(5)	3.314(5)
C(7) ··· C(16‴)	3.493(5)	3.450(4)
C(14) ··· C(12″)	3.505(5)	3.446(6)
C(15) ··· C(11″)	3.506(5)	3.450(6)
C(15) ··· C(12″)	3.530(5)	3.486(6)
C(16) ··· C(10″)	3.497(5)	3.458(7)
C(16) ··· C(11″)	3.313(5)	3.267(5)

TABLE 3 (*Continued*)

(*c*) Other intermolecular contacts[c, d]

N(3) ··· H(3$^{\mathrm{I}}$)	2.62(5)	2.520(5)
N(3) ··· C(5$^{\mathrm{I}}$)	3.384(5)	3.342(3)
C(4) ··· H(5$^{\mathrm{I}}$)	3.01(4)	2.806(8)
C(6) ··· H(4$^{\mathrm{I}}$)	2.92(4)	2.812(9)
C(9) ··· H(3$^{\mathrm{I}}$)	3.02(4)	2.880(5)
C(10) ··· H(3$^{\mathrm{I}}$)	3.11(4)	2.929(4)
C(11) ··· H(3$^{\mathrm{I}}$)	2.97(3)	2.781(6)
H(5) ··· H(3$^{\mathrm{I}}$)	2.64(4)	2.401(12)
C(3) ··· H(7$^{\mathrm{II}}$)	3.06(4)	2.854(9)
C(4) ··· H(7$^{\mathrm{II}}$)	2.95(4)	2.741(6)
H(2) ··· H(6$^{\mathrm{II}}$)	2.58(5)	2.384(6)
N(1) ··· H(7$^{\mathrm{III}}$)	3.13(3)	2.934(3)
H(1) ··· C(13$^{\mathrm{III}}$)	3.01(3)	2.794(9)
H(1) ··· C(14$^{\mathrm{III}}$)	3.23(4)	3.014(5)
H(1) ··· H(7$^{\mathrm{III}}$)	2.55(5)	2.350(14)
C(13) ··· H(8$^{\mathrm{IV}}$)	2.86(3)	2.671(5)
C(14) ··· H(8$^{\mathrm{IV}}$)	3.04(3)	2.835(8)
H(7) ··· H(8$^{\mathrm{IV}}$)	2.49(6)	2.373(7)

[a] 295 K distances are from ref. 1. Primed, double-primed, and triple-primed atoms are related by the co-ordinate transformations: $-x, -y, -z$; $x, -1 + y, z$; and $-x, 1 - y, -z$ respectively. [b] Corrected for thermal motion by the TSL rigid-body model described in the text. [c] All unique intermolecular contacts are given within the limits of the contact radii: Co, 2.1; N, C, 1.75; H, 1.25 Å. The 295 K contacts involving H are only approximate because H atoms are in refined (*X*-ray) and not idealised positions. [d] Roman numeral superscripts refer to the following co-ordinate transformations: I $-x, -\frac{1}{2} + y, \frac{1}{2} - z$; II $1 + x, \frac{3}{2} - y, \frac{1}{2} + z$; III $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$; IV $-1 - x, \frac{1}{2} + y, -\frac{1}{2} - z$.

An analysis of the 295 and 4.3 K intramolecular bond distances in [Co(pc)] (Table 3) indicates significant and systematic differences, with the 4.3 K bond distances being, in general, larger than the corresponding 295 K bond distances. The thermal-motion correction has the expected effect of increasing slightly the 295 K bond distances; however, the 4.3 K distances are in general still larger than these corrected distances and it is clear that some other effect is causing the discrepancies. An error in the determination of the cell parameters of [Co(pc)] at 4.3 K could cause a systematic increase in *all* the 4.3 K bond distances. However, the care with which the cell was determined, the fact that not all the 4.3 K distances are larger than the corresponding 295 K distances, and the reasonable C–H bond distances (Table 3) from the neutron-diffraction study indicate that the 4.3 K cell as determined is not in significant error.

The systematic differences in the bond lengths are particularly evident in the benzene-ring C–C distances, with the average benzene-ring C–C distance at 295 K being 1.383(1) whereas at 4.3 K it is 1.395(2) Å. The benzene-ring carbon atoms, in particular those with a hydrogen substituent, are very prone to refine to positions somewhat nearer the centre of the benzene ring than the true nuclear positions, in an *X*-ray diffraction analysis using data of only limited resolution.[12] This is because of an asymmetrical distribution of valence-electron density about the carbon atom, and the corresponding shift of the atom from its true nuclear position to the centroid of the surrounding electron density, with the subsequent reduction of the deformation charge density within the C–C bonds. The absence of deformation charge density in HC–CH bonds is well known, for instance in the analysis of diphenyl,[13] in which the inter-ring C–C bond has a high residual density but the hydrogen-substituted bonds show little deformation density in the molecular plane. This absence of bonding charge density is also observed in the *X*-ray analysis of benzene,[14] in which the mean C–C bond is 1.392 compared with the value obtained from neutron diffraction of 1.398 Å, and it is also evident in the charge-density analysis of [Mn(pc)].[15] This behaviour of benzene-ring carbon atoms has previously been discussed, and impressively demonstrated by theoretical modelling.[12] In the electron-density analysis of [Mn(pc)] at 116 K it was found [15] that, by placing small spherically symmetrical charges of *ca.* 0.2 e Å^{-3} at the midpoints of the C–C and C–N bonds during the refinement of the atomic positional parameters, the resultant atomic positions and bond distances were very much closer to those derived in the present neutron-diffraction study of [Co(pc)].

TABLE 4

Bond angles (°) * in [Co(pc)]

	295 K	4.3 K
N(2)–Co–N(4)	90.7(1)	91.3(1)
N(2)–Co–N(4′)	89.3(1)	88.7(1)
C(1)–N(1)–C(16′)	121.2(2)	120.8(1)
Co–N(2)–C(1)	127.2(2)	127.5(2)
Co–N(2)–C(8)	126.3(2)	125.4(1)
C(1)–N(2)–C(8)	106.6(2)	107.1(2)
C(8)–N(3)–C(9)	121.7(3)	121.7(3)
Co–N(4)–C(9)	125.7(2)	125.5(1)
Co–N(4)–C(16)	127.3(2)	127.8(2)
C(9)–N(4)–C(16)	106.9(2)	106.7(2)
N(1)–C(1)–N(2)	127.4(3)	127.9(3)
N(1)–C(1)–C(2)	122.8(2)	122.4(1)
N(2)–C(1)–C(2)	109.7(3)	109.7(3)
C(1)–C(2)–C(3)	132.7(3)	132.3(3)
C(1)–C(2)–C(7)	106.7(2)	106.4(2)
C(3)–C(2)–C(7)	120.6(3)	121.3(3)
C(2)–C(3)–C(4)	117.1(3)	116.8(3)
C(2)–C(3)–H(1)		122.0(5)
C(4)–C(3)–H(1)		121.1(4)
C(3)–C(4)–C(5)	122.3(3)	121.5(2)
C(3)–C(4)–H(2)		119.9(5)
C(5)–C(4)–H(2)		118.6(5)
C(4)–C(5)–C(6)	120.7(4)	121.4(3)
C(4)–C(5)–H(3)		119.2(2)
C(6)–C(5)–H(3)		119.4(3)
C(5)–C(6)–C(7)	117.1(3)	116.9(2)
C(5)–C(6)–H(4)		122.4(5)
C(7)–C(6)–H(4)		120.7(4)
C(2)–C(7)–C(6)	122.2(2)	122.1(2)
C(2)–C(7)–C(8)	106.3(3)	106.5(3)
C(6)–C(7)–C(8)	131.4(3)	131.5(2)
N(2)–C(8)–N(3)	127.6(2)	128.1(2)
N(2)–C(8)–C(7)	110.6(2)	110.2(2)
N(3)–C(8)–C(7)	121.8(3)	121.7(3)
N(3)–C(9)–N(4)	128.0(3)	127.9(2)
N(3)–C(9)–C(10)	121.7(3)	122.2(3)
N(4)–C(9)–C(10)	110.3(2)	109.9(2)
C(9)–C(10)–C(11)	131.9(3)	131.4(2)
C(9)–C(10)–C(15)	106.5(3)	106.8(3)
C(11)–C(10)–C(15)	121.7(2)	121.8(2)
C(10)–C(11)–C(12)	117.2(3)	117.3(3)
C(10)–C(11)–H(5)		121.0(3)
C(12)–C(11)–H(5)		121.7(5)
C(11)–C(12)–C(13)	120.9(4)	121.0(3)
C(11)–C(12)–H(6)		119.9(3)
C(13)–C(12)–H(6)		119.1(3)
C(12)–C(13)–C(14)	122.0(3)	121.2(2)
C(12)–C(13)–H(7)		118.9(5)
C(14)–C(13)–H(7)		119.9(5)
C(13)–C(14)–C(15)	117.0(3)	117.5(3)
C(13)–C(14)–H(8)		120.8(3)
C(15)–C(14)–H(8)		121.8(4)
C(10)–C(15)–C(14)	121.1(3)	121.2(3)
C(10)–C(15)–C(16)	106.5(2)	106.0(2)
C(14)–C(15)–C(16)	132.3(3)	132.8(3)
N(4)–C(16)–C(15)	109.8(3)	110.5(3)
N(4)–C(16)–N(1′)	127.5(3)	127.2(3)
C(15)–C(16)–N(1′)	122.7(2)	122.2(1)
N(2)–Co · · · N(3‴)	85.5(1)	85.7(1)
N(4)–Co · · · N(3‴)	90.3(1)	90.4(1)
C(8)–N(3) · · · Co‴	89.6(2)	89.9(2)
C(9)–N(3) · · · Co‴	95.5(2)	95.9(2)

* Prime and triple-prime superscripts refer to the co-ordinate transformations $-x, -y, -z$ and $-x, 1 - y, -z$ respectively. The 295 K angles are from ref. 1.

The well known apparent shift of the *X*-ray hydrogen-atom position toward the bonded atom is a result of the relatively large asymmetry of the hydrogen charge density. Similar but smaller effects, like that discussed above for benzene-ring systems, occur for first-row atoms in asymmetrical environments.[16] For example, the N–O distances in *p*-nitropyridine *N*-oxide are *ca.* 0.007 Å larger for the *X*-ray refinement at 30 K [$(\sin\theta)/\lambda \leqslant 1.0$ Å^{-1}] [17] than for the neutron-diffraction analysis at 30 K.[18] The main effect here is the shift of the oxygen atoms, in the *X*-ray refinement, towards the lone-pair density. In this case, the effects of the resolution of the *X*-ray data are strikingly illustrated by a high-order refinement, using only data above $(\sin\theta)/\lambda = 0.75$ Å^{-1}, which yields N–O bond distances essentially in agreement with the neutron-diffraction values.[18] The aromatic ring C–C and C–N distances in *p*-nitropyridine *N*-oxide from the 30 K *X*-ray refinement using all the data [$(\sin\theta)/\lambda \leqslant 1.0$ Å^{-1}] are in good agreement with the neutron-diffraction results, and this is generally found to be the case with *X*-ray data of high resolution. In such cases, the core and valence-electron densities can be resolved. However, a 298 K analysis of *p*-nitropyridine *N*-oxide, using *X*-ray data of limited resolution [$(\sin\theta)/\lambda \leqslant 0.76$ Å^{-1}],[17] indicates the problems faced in interpreting the chemical implications of such structure determinations. The 30 K neutron and high-resolution *X*-ray analyses clearly show the two hydrogen-substituted C–C bonds in the *para*-substituted aromatic ring to be slightly shorter (1.377 Å) than other C–C ring bonds, indicating a contribution of quinoid resonance structures. However, neglect of the asymmetrical valence-density effects about the hydrogen-substituted carbon atoms, in the 298 K refinement of limited resolution, suggests an apparently greater shortening of these C–C bonds, to a mean distance of 1.364 Å (after correction for thermal motion). A chemist, unaware of the limitations of refinements such as the latter, might be tempted to assume, for example, a greater degree of quinoid resonance than is actually the case.

In the 295 K *X*-ray analysis of [Co(pc)] discussed here [1] the data are of limited resolution [$(\sin\theta)/\lambda \leqslant 0.705$ Å^{-1}] in relation to the resolution required in accurate electron-density studies by *X*-ray diffraction. However, this limit of resolution is quite normal in routine *X*-ray structural analyses, and the present study serves to highlight the degree of inaccuracy in bond distances determined from such analyses. In particular, the systematic errors in bond distances, caused by neglect of the aspherical and asymmetrical nature of the valence-electron density, can be far greater than the least-squares determined standard deviations would indicate. Hence great care should be taken in the comparison of bond distances from structural analyses of different resolution.

The atomic positions obtained from the neutron-diffraction method are not affected significantly by the fact that the data are of only moderate extent because the atomic nuclei, responsible for the diffraction process, act as point scatterers, and are not affected by chemical bonding. This contrasts with the *X*-ray case where the scattering electron density has a root-mean-square (r.m.s.) width of *ca.* 1 Å which enhances the effects of random errors in the data, and where the centroid of the valence-charge density does not in general coincide with the nuclear position. Furthermore, at **4.3** K the thermal motion has a very small r.m.s. amplitude leading to an excellent definition of atomic positional co-ordinates from the present neutron-diffraction data for [Co(pc)] (within the limitation of the lack of resolution along the *b* axis direction due to inaccessible data). The thermal parameters obtained from the present neutron study are not correlated with effects such as aspherical valence-charge density, unlike the *X*-ray case; therefore, within the general limit of resolution of the data [$(\sin\theta)/\lambda \leqslant$ 0.736 $Å^{-1}$] and the low resolution along the *b* axis direction, the thermal parameters in Table 2 are believed to accurately represent the zero-point motion in [Co(pc)]. The low resolution along the *b* axis direction in the present data set may introduce systematic errors in the refined structure. To determine the significance of such errors is extremely difficult and no allowance has been made for them in the e.s.d.s quoted in the Tables.

Because the neutron-diffraction method yields the true nuclear positions, and there is no apparent bond shortening due to thermal vibrations at 4.3 K, the structural parameters from the present study are believed to more accurately portray the [Co(pc)] molecule, and little comparison can be made between the structure at 4.3 and that at 295 K. Perhaps the one worthwhile comparison is provided by the intermolecular contact distances (Table 3), which clearly indicate that the molecules pack more closely at lower temperature. In particular, the Co · · · N(3″) contact {where N(3″) is the ligand atom of a neighbouring molecule with which, in the proposed path for ferromagnetic exchange,[1] the Mn atom in [Mn(pc)] interacts} is **3.219(3)** at **295** compared with **3.154(3)** Å at **4.3** K. By comparison, this contact distance is considerably less in [Mn(pc)], having values of **3.169(6)** [1] and **3.148(2)** [15] Å at **295** and **116** K respectively. Some displacements from, and angles between, selected mean planes are presented in SUP 22789 for both **295** and **4.3** K analyses of [Co(pc)].

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