Structural Chemistry of Phthalocyaninato-cobalt(II) and -manganese(II)

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The crystal and molecular structures of the β-polymorphic forms of phthalocyaninatomanganese(II), [Mn(pc)], and phthalocyaninatocobalt(II), [Co(pc)], have been determined by single-crystal *X*-ray diffraction methods at 295 K, and also at 116 K in the case of [Mn(pc)]. Crystals are of the monoclinic β-polymorph type, space group $P2_1/c$, $Z = 2$; for [Mn(pc)] (116 K), $a = 14.590(3)$, $b = 4.741(1)$, $c = 19.301(5)$ Å, $\beta = 120.79(1)°$; (295 K), $a = 14.576(5)$, $b = 4.755(1)$, $c = 19.362(7)$ Å, $\beta = 120.70(2)°$; [Co(pc)] (295 K), $a = 14.542(2)$, $b = 4.773\,1(5)$, $c = 19.352(2)$ Å, $\beta = 120.824(7)°$. Automatic diffractometry has provided significant Bragg intensities for 1 608 {[Mn(pc)], 116 K}, 1 525 (295 K), and 1 930 {[Co(pc)]} independent reflections and the structures have been refined by full-matrix least-squares methods to *R* 0.038 {[Mn(pc)], 116 K}, 0.072 (295 K), and 0.039 {[Co(pc)]}. The metal atoms co-ordinate within the central cavity of the macrocyclic phthalocyaninate ligand to a precisely planar array of nitrogen atoms, with mean bond lengths Mn–N = 1.941(3) Å at 116 K, 1.933(5) Å at 295 K, and Co–N 1.908(2) Å. The intermolecular packing is of the typical herringbone arrangement, with angles of 47.9 {[Mn(pc)], 116 K} and 47.3° {[Co(pc)]} between the normals to the MN_4 co-ordination planes and the crystallographic *b* axes. Each molecule has close contacts with two neighbours related by translations of ±*b*, resulting in pseudo-octahedral metal environments with axial Mn–N contacts of 3.150(3) (116), 3.169(6) Å (295 K), and a Co–N contact of 3.219(3) Å. The importance of these intermolecular contacts in establishing a ferromagnetic exchange path in [Mn(pc)] is discussed, as are deviations within the macrocyclic ligand from D_{4h} symmetry.

THE now classical structural studies of the phthalocyanines by Robertson,[1-5] first reported in 1935, included the structure determination of the free phthalocyanine base (H_2pc) [2] and, in what was the first heavy-atom structure determination, of phthalocyaninatonickel(II), [Ni(pc)].[4] Metallophthalocyanines, together with metalloporphyrins and chlorins, have received much experimental and theoretical investigation of their geometrical structures largely on account of their generic relation to the naturally occurring porphyrins, chlorins, and corrins found as chromophores in haemoglobin, myoglobin, the cytochromes, chlorophylls, and vitamin B_{12}. Three well characterised polymorphic forms of the phthalocyanines [6] are distinguished by differences in crystal packing; there is no evidence for significant intramolecular differences between the polymorphs.[7] All the structures described and discussed below are of the common β-polymorph (monoclinic) type.

Phthalocyaninatomanganese(II), [Mn(pc)], is unusual in two ways: first it provides an almost unique example of the intermediate-spin state for Mn^{II}, $S = \frac{3}{2}$; secondly, it is a rare example of a ferromagnetic molecular crystal [8,9] ($T_c = 8.6$ K). Phthalocyaninatocobalt(II) (Co^{II}, $S = \frac{1}{2}$) remains a paramagnet at 4.2 K.[10] We have chosen these two compounds 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 analysis. This method relies on a detailed knowledge of the crystal and molecular structure; hence the reason for the present studies since no detailed diffraction analyses had been reported previously for [Mn(pc)] and [Co(pc)]. Both compounds are isomorphous with the metal-free H_2pc and with its iron(II), nickel(II), and copper(II) derivatives.[3] After the completion of our structure determination of [Mn(pc)], an independent *X*-ray study of this compound at 293 K was reported;[11] those results are in essential agreement with ours at 295 K. The results of our structure determination of [Mn(pc)] at 295 K are discussed briefly below, and analyses of [Co(pc)] at 295 K and of [Mn(pc)] at 116 K are detailed fairly fully.

EXPERIMENTAL

Single crystals suitable for diffraction studies were grown by entrainer vacuum sublimation under conditions already described.[12] Crystal data are presented in Table 1.

TABLE 1

Crystal data for [Mn(pc)] and [Co(pc)]

Compound	[Mn(pc)] $C_{32}H_{16}MnN_8$		[Co(pc)] $C_{32}H_{16}CoN_8$
M	567.49	567.49	571.48
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
T/K	295	116	295
a/Å	14.576(5)	14.590(3)	14.542(2)
b/Å	4.755(1)	4.741(1)	4.773 1(5)
c/Å	19.362(7)	19.301(5)	19.352(2)
β/°	120.70(2)	120.79(1)	120.824(7)
U/Å^3	1 153.9	1 146.9	1 153.5
Z	2	2	2
D_c/g cm^{-3}	1.633	1.643	1.645
λ(Mo-K_α)/Å	0.709 26	0.710 69	0.709 26
μ/cm^{-1} (ref. 13)	6.490	6.530	8.214
Crystal dimensions (mm)	0.04 × 0.10 × 0.53	0.04 × 0.10 × 0.53	0.10 × 0.16 × 0.26
Unique data	1 525 $I > 2\sigma(I)$	1 608 $I > 3\sigma(I)$	1 930 $I > 3\sigma(I)$
(sin θ)/λ limit (Å^{-1})	0.705	0.662	0.705
No. of variables	219	219	219

Oscillation and Weissenberg photographs at 295 K showed the crystals of [Mn(pc)] and [Co(pc)] to be of the monoclinic β-polymorph type. The space group $P2_1/c$ was determined in each case from the observed systematic absences. At 116 K the absences $0k0$ for k odd, and $h0l$ for l odd, were confirmed on the diffractometer. Unit-cell parameters, together with their estimated standard deviations (e.s.d.s),

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were derived in each case by a least-squares analysis of the setting angles determined for 12 (295 K) or 15 (116 K) angularly well separated reflections each with a 2θ value greater than 20°. Data at 295 K were obtained from a Hilger and Watts automatic four-circle diffractometer (Y290) using graphite-monochromatised Mo-K_α radiation (λ 0.709 26 Å). Data at 116 K were obtained from a Syntex $P2_1$ automatic four-circle diffractometer using a Syntex LT-1 low-temperature attachment and graphite-monochromatised Mo-K_α radiation (λ 0.710 69 Å); at the settings used, the temperature was estimated (by independent measurements) to be 116 ± 2 K. In each case, intensities were measured *via* an ω—2θ scan from crystals mounted with the *b* axis coincident with the ϕ diffractometer axis. The same crystal of [Mn(pc)] was used for intensity data collection at 295 and 116 K. In each data collection no significant variations in the intensities of three standard reflections were observed, and geometrical and absorption[13] corrections were applied to the integrated intensities.

Structure Determinations.—Initial atomic co-ordinates used in the asymmetric unit of structure {half the [M(pc)] molecule} were those reported for [Ni(pc)].[4] Least-squares refinement of atomic co-ordinates and anisotropic temperature factors was performed by use of the program CRYLSQ[14] in the full-matrix mode, the function minimised being $\Sigma w(\Delta F)^2$ where w is the weight assigned to the $|F_o|$ values and $\Delta F = |F_o| - |F_c|$. Difference-Fourier syntheses yielded the positions of all the hydrogen atoms in each case, and these were included in the scattering models and refined with variable isotropic thermal parameters. In each case, after absorption corrections had been applied to the intensity data, no significant change in the R factor was observed upon subsequent refinement. Weighting schemes of the following forms were introduced: for [Mn(pc)] (295 K), $w = (|F_o|/30)^2$ for $|F_o| \leqslant 30$, otherwise $w = (30/|F_o|)^2$; (116 K), $w = 1$ for $|F_o| \leqslant 50$, otherwise $w = (50/|F_o|)^2$; for [Co(pc)], $w = (2.4 - 0.12|F_o| + 0.002|F_o|^2)^{-1}$.

For [Mn(pc)] (295 K), refinement converged with $R\ (= \Sigma|\Delta F|/\Sigma|F_o|)$ 0.072 and $R'\ [= (\Sigma w\{\Delta F\}^2/\Sigma w|F_o|^2)^{1/2}]$ 0.061. The maximum parameter shift-to-error ratio at convergence was 0.06 : 1. A final difference synthesis was essentially featureless and showed no peaks $>|0.7|$ e Å^{-3}. At 116 K refinement converged with R 0.038 and R' 0.044. The maximum shift-to-error ratio at convergence was 0.005 : 1. A final difference synthesis was essentially featureless and showed no peaks $>|0.5|$ e Å^{-3}. For [Co(pc)], refinement converged with R 0.039 and R' 0.040; the maximum shift-to-error ratio was 0.2 : 1. A final difference synthesis was essentially featureless and showed no peaks $>|0.4|$ e Å^{-3}.

Final atomic positional co-ordinates and thermal parameters, with e.s.d.s in parentheses, are listed in Tables 2 and 3 for [Mn(pc)] (295 and 116 K) and in Tables 4 and 5 for [Co(pc)]. Atomic scattering-factor curves for non-hydrogen atoms were taken from ref. 15*a*, with those for Mn and Co modified for the real and imaginary anomalous dispersion corrections.[15b] The scattering-factor curve for H was taken from ref. 16. All the computations were performed on an ICL 1906 computer at the Atlas Computer Laboratory. Initial data processing used the University of Sussex computer programs, and structure determination and refinement used the '*X*-Ray '74' program system.[14] Observed and calculated structure factors for [Mn(pc)] (116 K) and [Co(pc)] are listed in Supplementary Publication No. SUP 22414 (21 pp.).*

DISCUSSION

Molecular Stereochemistries.—The molecular geometries and atom numbering of the centrosymmetric [Mn(pc)] (116 K) and [Co(pc)] molecules are shown in Figures 1 and 2. Interatomic distances, angles, and correlated e.s.d.s are given in Tables 6 and 7 for [Mn(pc)] (295 and 116 K) and for [Co(pc)]. In both compounds

TABLE 2

Final atomic positional co-ordinates for [Mn(pc)] *

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Mn	0	0	0
N(1)	0.252 9(2)	0.029 3(7)	0.161 2(1)
	0.252 1(3)	0.030 4(13)	0.160 1(3)
N(2)	0.073 3(2)	0.225 4(6)	0.097 4(2)
	0.072 8(3)	0.222 9(10)	0.096 9(3)
N(3)	−0.072 0(2)	0.529 9(7)	0.077 5(2)
	−0.072 5(3)	0.526 4(13)	0.077 3(3)
N(4)	−0.132 5(2)	0.199 9(6)	−0.033 5(2)
	−0.132 0(3)	0.197 9(10)	−0.033 3(2)
C(1)	0.179 9(2)	0.201 8(7)	0.158 8(2)
	0.179 8(4)	0.199 8(13)	0.158 6(3)
C(2)	0.200 6(3)	0.402 1(7)	0.222 0(2)
	0.199 3(4)	0.399 6(12)	0.220 9(3)
C(3)	0.291 7(3)	0.458 0(8)	0.296 8(2)
	0.289 9(5)	0.456 5(16)	0.295 4(3)
C(4)	0.283 3(3)	0.662 4(8)	0.344 4(2)
	0.282 1(5)	0.658 3(15)	0.342 5(4)
C(5)	0.188 2(3)	0.807 1(8)	0.319 3(2)
	0.186 9(5)	0.801 4(17)	0.317 4(4)
C(6)	0.097 9(3)	0.754 1(8)	0.245 1(2)
	0.096 6(5)	0.748 0(15)	0.244 3(4)
C(7)	0.105 7(2)	0.547 6(7)	0.196 9(2)
	0.105 0(4)	0.543 9(14)	0.195 8(3)
C(8)	0.027 6(3)	0.436 4(7)	0.119 0(2)
	0.027 6(4)	0.434 2(11)	0.118 8(3)
C(9)	−0.145 3(3)	0.415 4(7)	0.008 8(2)
	−0.145 1(4)	0.414 6(11)	0.009 1(3)
C(10)	−0.256 2(2)	0.503 1(9)	−0.033 2(2)
	−0.256 1(4)	0.499 0(17)	−0.033 3(3)
C(11)	−0.310 0(3)	0.703 8(8)	−0.014 3(2)
	−0.309 2(5)	0.702 1(14)	−0.013 6(4)
C(12)	−0.418 8(3)	0.731 7(8)	−0.067 2(2)
	−0.417 8(6)	0.726 0(16)	−0.066 5(4)
C(13)	−0.472 2(3)	0.568 3(8)	−0.136 7(2)
	−0.470 5(5)	0.566 0(15)	−0.135 9(4)
C(14)	−0.418 9(3)	0.369 1(8)	−0.155 8(2)
	−0.417 2(5)	0.368 0(14)	−0.154 8(4)
C(15)	−0.309 4(3)	0.338 5(7)	−0.102 4(2)
	−0.308 8(4)	0.337 2(12)	−0.102 4(3)
C(16)	−0.230 9(2)	0.150 7(7)	−0.102 8(2)
	−0.230 8(4)	0.150 6(13)	−0.102 9(3)
H(1)	0.357(3)	0.363(8)	0.313(2)
	0.350(5)	0.376(12)	0.303(3)
H(2)	0.349(3)	0.708(8)	0.399(2)
	0.348(4)	0.688(13)	0.395(3)
H(3)	0.185(3)	0.951(9)	0.353(2)
	0.177(4)	0.918(11)	0.346(3)
H(4)	0.034(3)	0.846(7)	0.228(2)
	0.026(5)	0.823(14)	0.224(3)
H(5)	−0.275(3)	0.820(8)	0.030(2)
	−0.273(4)	0.791(12)	0.036(3)
H(6)	−0.460(3)	0.871(9)	−0.057(2)
	−0.455(6)	0.840(18)	−0.059(5)
H(7)	−0.549(3)	0.597(9)	−0.174(2)
	−0.546(5)	0.591(13)	−0.176(4)
H(8)	−0.455(3)	0.260(8)	−0.202(2)
	−0.452(4)	0.256(14)	−0.202(3)

* Upper and lower values quoted are for structure refinements at 116 and 295 K respectively.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

the metal atoms have essentially D_{4h} symmetry but the small significant deviations from ligand planarity and D_{4h} symmetry are of considerable interest. Intraligand bond lengths and angles, including systematic variations of the benzene-ring angles from the hexagonal value, agree well with the values determined in other phthalocyanine structures.[11,17-19]

TABLE 3

Final atomic thermal parameters for [Mn(pc)]. Upper and lower values quoted are for structure refinements at 116 and 295 K respectively, U tensors in Å^2. 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 $T = \exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$ respectively

Atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Mn	13.6(3)	17.4(3)	15.7(3)	1.7(4)	6.9(2)	−2.5(4)
	22.7(6)	23.5(7)	24.8(6)	2.6(8)	9.7(5)	−3.4(8)
N(1)	16(1)	20(1)	19(1)	−2(1)	8(1)	−1(1)
	27(2)	28(3)	31(2)	−1(3)	16(2)	−7(3)
N(2)	17(1)	18(1)	18(1)	2(1)	10(1)	0(1)
	28(3)	25(3)	27(2)	−1(2)	16(2)	−3(2)
N(3)	20(1)	22(2)	20(1)	3(1)	12(1)	0(1)
	32(2)	27(3)	33(2)	5(3)	20(2)	−2(3)
N(4)	17(1)	15(1)	19(1)	2(1)	10(1)	0(1)
	26(2)	24(3)	25(2)	3(2)	14(2)	−2(2)
C(1)	16(1)	21(2)	18(1)	−2(1)	9(1)	1(1)
	28(3)	27(3)	28(3)	−5(3)	12(3)	−1(3)
C(2)	18(2)	16(1)	22(2)	−3(1)	13(1)	2(1)
	27(3)	26(3)	31(3)	−4(2)	17(2)	1(3)
C(3)	20(2)	25(2)	22(2)	−4(2)	11(1)	−1(1)
	30(3)	37(5)	34(3)	−5(3)	15(3)	−5(3)
C(4)	24(2)	31(2)	21(2)	−8(2)	12(1)	−3(2)
	36(3)	42(4)	28(3)	−12(3)	15(3)	−9(3)
C(5)	29(2)	26(2)	25(2)	−8(2)	18(2)	−7(2)
	48(4)	47(5)	40(4)	−11(4)	31(3)	−19(4)
C(6)	20(2)	23(2)	26(2)	0(1)	15(1)	−1(1)
	32(3)	36(4)	39(4)	−2(3)	22(3)	0(3)
C(7)	22(2)	20(2)	20(2)	−5(1)	13(1)	−1(1)
	31(3)	28(4)	26(3)	−3(3)	17(2)	−3(3)
C(8)	19(2)	18(2)	21(1)	1(1)	14(1)	2(1)
	24(3)	27(4)	29(3)	−5(2)	15(2)	−2(2)
C(9)	18(2)	17(2)	21(2)	0(1)	11(1)	2(1)
	26(3)	19(3)	25(3)	3(2)	13(2)	6(2)
C(10)	18(1)	20(1)	19(1)	0(2)	12(1)	4(2)
	33(3)	26(3)	35(3)	5(4)	22(2)	12(4)
C(11)	24(2)	20(2)	23(2)	3(2)	13(1)	0(1)
	30(3)	34(4)	31(3)	6(3)	14(3)	−1(3)
C(12)	22(2)	29(2)	33(2)	9(2)	16(2)	4(2)
	43(4)	39(4)	49(4)	12(4)	26(3)	2(4)
C(13)	19(2)	31(2)	28(2)	6(1)	10(1)	5(1)
	24(3)	48(5)	45(4)	11(3)	11(3)	10(3)
C(14)	19(2)	26(2)	22(2)	1(1)	9(1)	0(1)
	27(3)	33(4)	40(4)	1(3)	16(3)	−2(3)
C(15)	21(2)	18(2)	19(1)	3(1)	13(1)	4(1)
	28(3)	21(3)	29(3)	4(3)	17(2)	6(3)
C(16)	17(1)	19(2)	18(1)	0(1)	10(1)	5(1)
	25(3)	29(3)	25(3)	−1(3)	12(2)	3(3)
H(1)	18(9)					
	26(17)					
H(2)	20(10)					
	24(15)					
H(3)	28(11)					
	20(16)					
H(4)	8(8)					
	36(17)					
H(5)	16(9)					
	15(14)					
H(6)	33(11)					
	66(27)					
H(7)	28(11)					
	45(20)					
H(8)	20(9)					
	34(17)					

The Mn–N bond lengths in [Mn(pc)] at 116 K [average 1.941(3) Å] are identical within experimental errors with those found at 295 K [average 1.933(5) Å] and with those previously reported[11] at 293 K [average 1.938(3) Å]; the Co–N bond distances in [Co(pc)] [average 1.908(2) Å] agree with the less accurate values reported for a di-adduct of [Co(pc)] [average Co–N 1.914(8) Å].[20] The

TABLE 4

Final atomic positional co-ordinates for [Co(pc)]

Atom	x/a	y/b	z/c
Co	0	0	0
N(1)	0.251 4(2)	0.026 8(6)	0.159 7(1)
N(2)	0.071 8(2)	0.217 8(5)	0.096 0(1)
N(3)	−0.072 1(2)	0.516 8(7)	0.078 5(1)
N(4)	−0.130 7(2)	0.194 7(5)	−0.032 6(1)
C(1)	0.177 9(2)	0.195 7(6)	0.156 9(2)
C(2)	0.199 8(2)	0.393 6(6)	0.220 5(2)
C(3)	0.290 6(2)	0.449 8(7)	0.294 2(2)
C(4)	0.282 1(3)	0.651 9(8)	0.341 5(2)
C(5)	0.187 5(3)	0.795 4(8)	0.317 4(2)
C(6)	0.097 0(2)	0.740 6(7)	0.243 8(2)
C(7)	0.105 5(2)	0.537 3(7)	0.196 3(2)
C(8)	0.027 3(2)	0.424 3(6)	0.118 5(2)
C(9)	−0.144 4(2)	0.404 8(6)	0.009 5(2)
C(10)	−0.255 1(2)	0.495 7(8)	−0.032 3(2)
C(11)	−0.308 0(2)	0.694 2(7)	−0.013 4(2)
C(12)	−0.416 4(3)	0.727 4(8)	−0.066 7(2)
C(13)	−0.469 3(2)	0.566 0(7)	−0.135 8(2)
C(14)	−0.416 8(2)	0.368 8(7)	−0.155 1(2)
C(15)	−0.308 1(2)	0.335 8(6)	−0.101 6(2)
C(16)	−0.228 7(2)	0.150 7(6)	−0.101 2(2)
H(1)	0.355(2)	0.361(7)	0.310(2)
H(2)	0.343(2)	0.694(8)	0.393(2)
H(3)	0.183(3)	0.930(7)	0.352(2)
H(4)	0.030(2)	0.843(7)	0.225(2)
H(5)	−0.272(2)	0.807(7)	0.032(2)
H(6)	−0.455(3)	0.860(8)	−0.054(2)
H(7)	−0.544(3)	0.594(7)	−0.173(2)
H(8)	−0.453(2)	0.263(7)	−0.204(2)

TABLE 5

Final atomic thermal parameters for [Co(pc)], U tensors in Å^2. Anisotropic and isotropic thermal parameters are defined as in Table 3

Atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Co	24.9(2)	22.1(2)	26.4(2)	0.7(3)	13.9(2)	−1.4(3)
N(1)	29(1)	29(1)	32(1)	−1(1)	15(1)	−1(1)
N(2)	28(1)	23(1)	26(1)	−1(1)	14(1)	−2(1)
N(3)	32(1)	30(1)	34(1)	4(1)	19(1)	−2(1)
N(4)	25(1)	25(1)	28(1)	1(1)	14(1)	0(1)
C(1)	28(1)	24(1)	30(1)	−3(1)	16(1)	−2(1)
C(2)	31(1)	28(1)	30(1)	−5(1)	17(1)	−2(1)
C(3)	33(1)	36(2)	36(1)	−5(1)	16(1)	−5(1)
C(4)	39(2)	47(2)	32(2)	−15(2)	17(1)	−13(2)
C(5)	49(2)	42(2)	38(2)	−13(2)	29(2)	−13(2)
C(6)	39(2)	36(2)	36(2)	−3(1)	24(1)	−5(1)
C(7)	33(1)	25(2)	28(1)	−5(1)	18(1)	−3(1)
C(8)	30(1)	24(1)	32(1)	−2(1)	19(1)	−2(1)
C(9)	30(1)	27(1)	28(1)	2(1)	17(1)	1(1)
C(10)	30(1)	29(1)	31(1)	5(2)	17(1)	7(2)
C(11)	39(2)	34(2)	37(2)	8(1)	21(1)	1(1)
C(12)	37(2)	43(2)	52(2)	14(2)	25(2)	5(2)
C(13)	29(1)	47(2)	45(2)	10(1)	15(1)	6(2)
C(14)	32(2)	38(2)	39(2)	3(1)	16(1)	−1(2)
C(15)	29(1)	28(2)	34(1)	4(1)	19(1)	4(1)
C(16)	27(1)	25(1)	31(1)	1(1)	15(1)	3(1)
H(1)	35(9)					
H(2)	38(9)					
H(3)	43(10)					
H(4)	32(9)					
H(5)	34(9)					
H(6)	58(11)					
H(7)	44(10)					
H(8)	34(9)					

average M–N distances observed in a sequence of metallophthalocyanines as a function of atomic number are summarised in Table 8. The systematic decrease in M–N bond distances from Mn^{II} to Ni^{II} is consistent with expectations based on variations in the effective nuclear charge; this trend is broken for Cu^{II} and Zn^{II} for reasons that simple crystal-field theory anticipates. The two chemically but non-crystallographically equivalent M–N distances of the metallophthalocyanines listed in Table 8 are identical within experimental error, but in H_2pc (where M represents the centre of inversion of the molecule) the two M–N distances are not equivalent, a feature probably representative of steric crowding due to

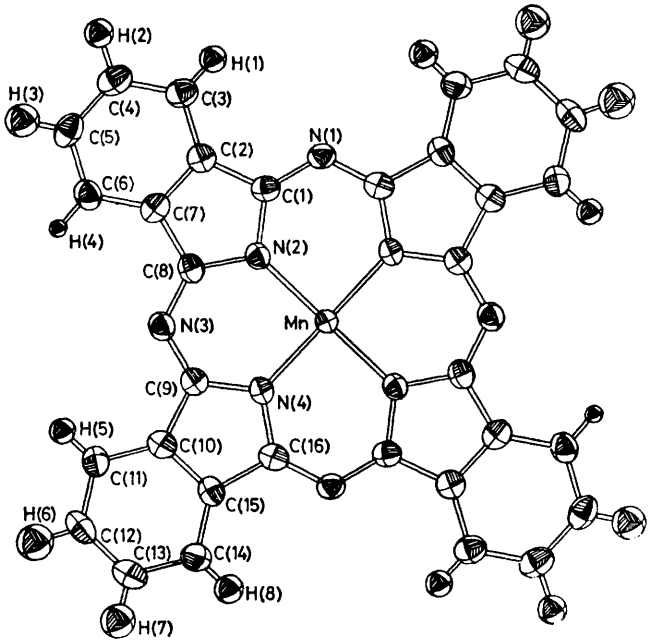

FIGURE 1 An ORTEP drawing of [Mn(pc)] (116 K parameters) showing the molecular geometry and atom numbering. The thermal ellipsoids are drawn at the 75% probability level

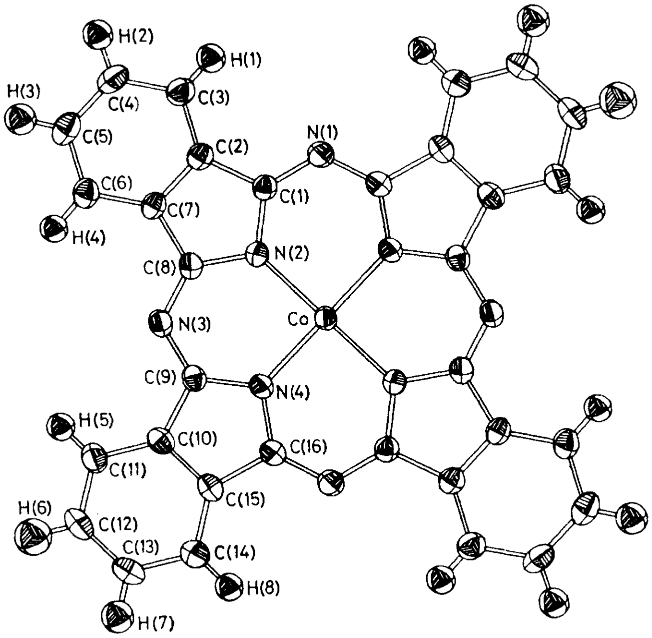

FIGURE 2 An ORTEP drawing of [Co(pc)] showing the molecular geometry and atom numbering. The thermal ellipsoids are drawn at the 50% probability level

TABLE 6

Interatomic distances (Å) in [Mn(pc)] and [Co(pc)]

Intramolecular distances [a]

	[Mn(pc)]		
	295 K	116 K	[Co(pc)]
M–N(2)	1.933(4)	1.939(3)	1.906(2)
M–N(4)	1.933(5)	1.942(3)	1.909(2)
N(1)–C(1)	1.315(9)	1.325(5)	1.318(4)
N(1)–C(16′)	1.308(8)	1.316(4)	1.313(4)
N(2)–C(1)	1.403(6)	1.396(3)	1.385(3)
N(2)–C(8)	1.382(9)	1.380(5)	1.368(4)
N(3)–C(8)	1.330(7)	1.326(4)	1.318(4)
N(3)–C(9)	1.312(6)	1.321(4)	1.318(3)
N(4)–C(9)	1.391(8)	1.379(5)	1.369(4)
N(4)–C(16)	1.399(6)	1.392(3)	1.378(3)
C(1)–C(2)	1.446(9)	1.450(5)	1.451(4)
C(2)–C(3)	1.397(7)	1.399(4)	1.386(3)
C(2)–C(7)	1.383(8)	1.393(5)	1.383(4)
C(3)–C(4)	1.369(11)	1.384(6)	1.378(5)
C(4)–C(5)	1.391(10)	1.393(5)	1.386(5)
C(5)–C(6)	1.378(7)	1.385(4)	1.381(4)
C(6)–C(7)	1.398(10)	1.396(6)	1.384(5)
C(7)–C(8)	1.432(7)	1.444(4)	1.448(3)
C(9)–C(10)	1.447(7)	1.451(4)	1.449(4)
C(10)–C(11)	1.408(11)	1.395(6)	1.383(5)
C(10)–C(15)	1.386(8)	1.391(4)	1.385(4)
C(11)–C(12)	1.383(8)	1.386(4)	1.381(4)
C(12)–C(13)	1.386(10)	1.391(5)	1.385(5)
C(13)–C(14)	1.384(11)	1.388(6)	1.379(6)
C(14)–C(15)	1.382(7)	1.397(4)	1.385(4)
C(15)–C(16)	1.447(9)	1.453(5)	1.452(5)
H(1)–C(3)	0.90(7)	0.95(4)	0.92(3)
H(2)–C(4)	0.99(4)	1.02(3)	0.95(3)
H(3)–C(5)	0.84(7)	0.96(5)	0.95(4)
H(4)–C(6)	0.97(7)	0.92(4)	0.97(3)
H(5)–C(11)	0.92(5)	0.93(3)	0.93(3)
H(6)–C(12)	0.83(10)	0.97(5)	0.96(5)
H(7)–C(13)	0.98(6)	0.98(4)	0.96(3)
H(8)–C(14)	0.95(6)	0.93(4)	0.96(3)
M ··· N(1)	3.392(4)	3.400(2)	3.370(2)
M ··· N(3)	3.352(6)	3.356(3)	3.336(3)
N(2) ··· N(4)	2.757(5)	2.765(3)	2.714(3)
N(2) ··· N(4′)	2.710(8)	2.724(4)	2.681(4)

Intermolecular contacts perpendicular to molecular plane [a,b]

	[Mn(pc)]		
	295 K	116 K	[Co(pc)]
M ··· N(3″)	3.169(6)	3.150(3)	3.219(3)
M ··· C(8″)	3.427(6)	3.410(3)	3.469(3)
M ··· C(9″)	3.554(6)	3.546(4)	3.593(3)
N(1) ··· C(2″)	3.450(9)	3.423(5)	3.463(4)
N(1) ··· C(7″)	3.456(9)	3.437(5)	3.466(5)
N(1) ··· C(10‴)	3.343(9)	3.338(5)	3.379(5)
N(1) ··· C(15‴)	3.452(9)	3.450(5)	3.486(4)
N(2) ··· C(6″)	3.515(9)	3.494(5)	3.526(4)
N(2) ··· N(4‴)	3.305(7)	3.283(4)	3.344(4)
N(2) ··· C(9‴)	3.240(9)	3.225(5)	3.276(5)
N(4) ··· C(8‴)	3.268(9)	3.258(5)	3.302(5)
C(1) ··· C(6″)	3.301(11)	3.280(6)	3.310(5)
C(1) ··· C(7″)	3.498(10)	3.485(5)	3.520(5)
C(1) ··· C(10‴)	3.452(10)	3.440(6)	3.468(5)
C(1) ··· C(15‴)	3.414(10)	3.406(6)	3.437(5)
C(1) ··· C(16‴)	3.474(9)	3.459(5)	3.501(4)
C(2) ··· C(5″)	3.458(10)	3.445(6)	3.469(5)
C(2) ··· C(16‴)	3.328(10)	3.320(6)	3.352(5)
C(7) ··· C(16‴)	3.475(10)	3.475(6)	3.493(5)
C(14) ··· C(12″)	3.501(11)	3.472(6)	3.505(5)
C(15) ··· C(11″)	3.476(9)	3.459(5)	3.506(5)
C(16) ··· C(10″)	3.472(10)	3.446(5)	3.497(5)

TABLE 6 (*Continued*)

Other intermolecular contacts [b,c]

	[Mn(pc)] 295 K	[Mn(pc)] 116 K	[Co(pc)]
C(16) ··· C($11''$)	3.296(11)	3.279(6)	3.313(5)
N(3) ··· H(3^{I})	2.67(7)	2.63(5)	2.62(5)
N(3) ··· C(5^{I})	3.399(11)	3.378(6)	3.384(5)
C(4) ··· H(5^{I})	2.99(6)	2.97(4)	3.01(4)
C(6) ··· H(4^{I})	2.96(8)	2.96(4)	2.92(4)
C(9) ··· H(3^{I})	3.07(7)	3.02(5)	3.02(4)
C(11) ··· H(3^{I})	3.11(5)	2.94(4)	2.97(3)
H(2) ··· H(6^{II})	2.54(11)	2.50(6)	2.58(5)
C(3) ··· H(7^{II})	3.05(7)	2.97(4)	3.06(4)
C(4) ··· H(7^{II})	2.96(9)	2.89(5)	2.95(4)
H(1) ··· H(7^{III})	2.60(9)	2.52(6)	2.55(5)
H(1) ··· C(13^{III})	3.08(6)	2.98(4)	3.01(3)
H(7) ··· H(8^{IV})	2.47(11)	2.53(7)	2.49(6)
C(13) ··· H(8^{IV})	2.89(6)	2.87(4)	2.86(3)
C(14) ··· H(8^{IV})	3.06(6)	3.03(4)	3.04(3)

[a] 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] All intermolecular contacts are given within the limits of the contact radii: Mn, Co, 2.1; N, C, 1.75; H, 1.25 Å. Contacts involving H are only approximate because H atoms are in refined and not idealised positions. [c] 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 $-1 - x, \frac{1}{2} + y, -\frac{1}{2} - z$.

the two disordered hydrogen atoms within the central macrocyclic cavity.[19] It is perhaps significant in this regard that the 'half-hydrogen' atom with the larger of the two least-squares-determined occupancy factors [0.64(2), 0.42(2)] [19] is associated with the pyrrole nitrogen atom positioned further from the centre of the cavity.

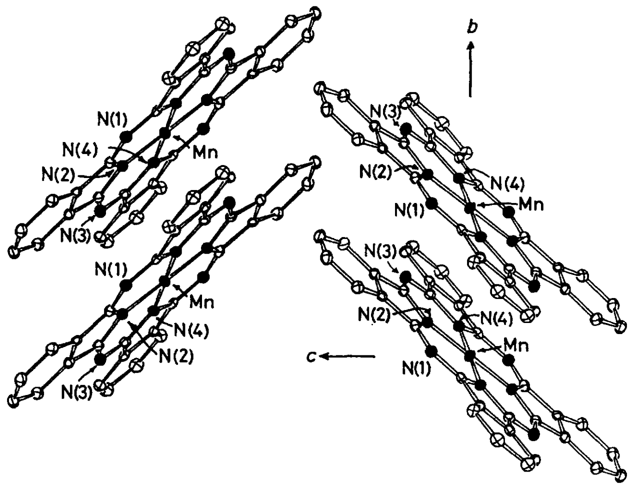

FIGURE 3 An ORTEP drawing, viewed along a^*, showing four molecules of [Mn(pc)] (116 K parameters) in the characteristic herringbone stacking. Mn and N atoms are shaded

TABLE 7

Bond angles (°) in [Mn(pc)] and [Co(pc)]

Angle *	[Mn(pc)] 295 K	[Mn(pc)] 116 K	[Co(pc)]
N(2)–M–N(4)	91.0(2)	90.9(1)	90.7(1)
N(2)–M–N($4'$)	89.0(2)	89.1(1)	89.3(1)
C(1)–N(1)–C($16'$)	122.9(4)	122.1(2)	121.2(2)
M–N(2)–C(1)	127.2(4)	126.9(3)	127.2(2)
M–N(2)–C(8)	125.8(3)	125.5(2)	126.3(2)
C(1)–N(2)–C(8)	107.0(4)	107.6(3)	106.6(2)
C(8)–N(3)–C(9)	123.2(6)	122.8(3)	121.7(3)
M–N(4)–C(9)	125.3(3)	125.3(2)	125.7(2)
M–N(4)–C(16)	127.1(4)	126.8(2)	127.3(2)
C(9)–N(4)–C(16)	107.6(5)	107.9(3)	106.9(2)
N(1)–C(1)–N(2)	126.6(5)	127.3(3)	127.4(3)
N(1)–C(1)–C(2)	124.8(4)	123.9(2)	122.8(2)
N(2)–C(1)–C(2)	108.5(5)	108.9(3)	109.7(3)
C(1)–C(2)–C(3)	131.9(6)	132.1(3)	132.7(3)
C(1)–C(2)–C(7)	107.3(4)	106.9(2)	106.7(2)
C(3)–C(2)–C(7)	120.8(6)	121.0(3)	120.6(3)
C(2)–C(3)–C(4)	117.9(6)	117.2(3)	117.1(3)
C(3)–C(4)–C(5)	121.1(5)	121.7(3)	122.3(3)
C(4)–C(5)–C(6)	121.9(7)	121.4(4)	120.7(4)
C(5)–C(6)–C(7)	116.9(6)	117.2(3)	117.1(3)
C(2)–C(7)–C(6)	121.4(4)	121.5(3)	122.2(2)
C(2)–C(7)–C(8)	107.3(6)	107.1(3)	106.3(3)
C(6)–C(7)–C(8)	131.3(5)	131.4(3)	131.4(3)
N(2)–C(8)–N(3)	127.0(5)	127.6(3)	127.6(2)
N(2)–C(8)–C(7)	109.8(5)	109.5(3)	110.6(2)
N(3)–C(8)–C(7)	123.1(6)	122.9(3)	121.8(3)
N(3)–C(9)–N(4)	127.7(5)	127.8(3)	128.0(3)
N(3)–C(9)–C(10)	123.6(6)	122.7(3)	121.7(3)
N(4)–C(9)–C(10)	108.7(4)	109.4(2)	110.3(2)
C(9)–C(10)–C(11)	130.3(5)	131.7(3)	131.9(3)
C(9)–C(10)–C(15)	107.6(6)	106.8(3)	106.5(3)
C(11)–C(10)–C(15)	122.1(5)	121.5(3)	121.7(2)
C(10)–C(11)–C(12)	115.8(6)	117.3(3)	117.2(3)
C(11)–C(12)–C(13)	122.1(8)	121.5(4)	120.9(4)
C(12)–C(13)–C(14)	121.5(6)	121.4(3)	122.0(3)
C(13)–C(14)–C(15)	117.6(6)	117.4(3)	117.0(3)
C(10)–C(15)–C(14)	120.9(6)	121.0(4)	121.1(3)
C(10)–C(15)–C(16)	107.2(4)	107.2(3)	106.5(2)
C(14)–C(15)–C(16)	131.9(6)	131.8(3)	132.3(3)
N(4)–C(16)–C(15)	108.7(5)	108.7(3)	109.8(3)
N(4)–C(16)–N($1'$)	127.1(6)	127.7(3)	127.5(3)
C(15)–C(16)–N($1'$)	124.1(4)	123.6(2)	122.7(2)
N(2)–M ··· N($3'''$)	85.3(2)	85.3(1)	85.5(1)
N(4)–M ··· N($3'''$)	90.6(2)	90.8(1)	90.3(1)
C(8)–N(3) ··· M'''	89.5(4)	89.6(2)	89.6(2)
C(9)–N(3) ··· M'''	96.0(4)	96.2(2)	95.5(2)

* Prime and triple-prime superscripts refer to the co-ordinate transformations $(-x, -y, -z)$ and $(-x, 1 - y, -z)$ respectively.

Intermolecular Arrangements and Related Matters.—The molecules of [Mn(pc)] and [Co(pc)] pack in similar

TABLE 8

M–N Bond distances and angles and intramolecular M ··· N separations in selected phthalocyanines [a]

Compound	M–N distance/Å	Angle/° N(2)–M–N(4)	Angle/° N(2)–M–N($4'$)	Separation/Å M ··· N(1)	Separation/Å M ··· N(3)
[Mn(pc)] (116 K)	1.941(3)	90.9(1)	89.1(1)	3.400(2)	3.356(3)
(295 K)	1.933(5)	91.0(2)	89.0(2)	3.392(4)	3.352(6)
[Fe(pc)] [11,b]	1.927(2)	90.9(1)	89.1(1)	3.388(1)	3.348(2)
[Co(pc)]	1.908(2)	90.7(1)	89.3(1)	3.370(2)	3.336(3)
[Ni(pc)] [4]	*ca.* 1.83				
[Cu(pc)] [17,b]	1.935(6)	91.3(2)	88.7(2)	3.388(4)	3.333(6)
[Zn(pc)] [18,b]	1.979(2)	91.0(1)	89.0(1)	3.401(2)	3.357(2)
H_2pc [19,c]	1.978(3), 1.955(3)	92.6(1)	87.4(1)	3.420(2)	3.325(3)

[a] Primed atoms are related to the unprimed atoms by the centre of inversion. [b] Values calculated using reported atomic co-ordinates. [c] Values calculated assuming M at the origin and using reported atomic co-ordinates.

fashion, the packing arrangement viewed perpendicular to the *b* axis being shown in Figure 3. The angles between the *b* axes and the normals to the planes through the MN_4 co-ordination groups of various phthalocyanines are given in Table 9. The probable path for magnetic superexchange in [Mn(pc)] is by spin delocalisation from the central Mn atom into the π system of the ligand and on to the N(3) atom in particular. The manganese atom lies relatively close [3.150(3) at 116, 3.169(6) Å at 295 K] to two N(3) atoms of neighbouring molecules which are related by translations of $\pm b$ to the original molecule, and the Mn $\cdots$ N(3''),N(3''') [the double and triple prime superscripts refer to atoms related to the unprimed atom by the operations $(x,\ -1+y,\ z)$ and $(-x,\ 1-y,\ -z)$ respectively] contact is at 4.7—4.8° to the normal to the plane containing Mn and the four co-ordinated N atoms. In contrast, the corresponding M $\cdots$ N(3''),N(3''') distances in other phthalocyanines are significantly greater (Table 10).

TABLE 9

Angles (°) between the *b* axes and the normals to the MN_4 co-ordination planes in selected phthalocyanines

Compound	
[Mn(pc)] (116 K)	47.9
(295 K)	47.7
[Fe(pc)] [11,*]	47.3
[Co(pc)]	47.3
[Cu(pc)] [17,*]	46.5
[Zn(pc)] [18,*]	48.4
H_2pc [19,*]	45.7

* Values calculated using reported atomic co-ordinates.

TABLE 10

Metal–nitrogen axial contact distances and angles in some phthalocyanines

Compound	M $\cdots$ N(3''),N(3''') distance [a]/Å	Angle (°) of M . . . N(3''),N(3''') contact to normal of the MN_4 co-ordination plane
[Mn(pc)] (116 K)	3.150(3)	4.8
(295 K)	3.169(6)	4.7
[Fe(pc)] [11,b]	3.237(2)	4.6
[Co(pc)]	3.219(3)	4.6
[Cu(pc)] [17,b]	3.283(6)	3.8
[Zn(pc)] [18,b]	3.231(2)	5.7
H_2pc [19,c]	3.317(3)	3.3

[a] Double- and triple-prime superscripts refer to atoms related to the unprimed atom by the operations $(x,\ -1+y,\ z)$ and $(-x,\ 1-y,\ -z)$ respectively. [b] Values calculated using reported atomic co-ordinates. [c] Values calculated assuming M at the origin and using reported atomic co-ordinates.

Deviations from D_{4h} symmetry within the co-ordination group are indicated by small but significant differences from 90° in the angles N(2)–M–N(4) and N(2)–M–N(4') [where N(4') is related to N(4) by the inversion centre]. These angles, together with the M $\cdots$ N(1) and M $\cdots$ N(3) intramolecular separations, are given in Table 8. The deviations from D_{4h} symmetry in the metallophthalocyanines are consequences of the packing adopted by the molecules within the crystal lattice, it being evident that an increase in the N(2)–M–N(4) angle from 90° is causally related to a decrease of the M $\cdots$ N(3) intramolecular distance.

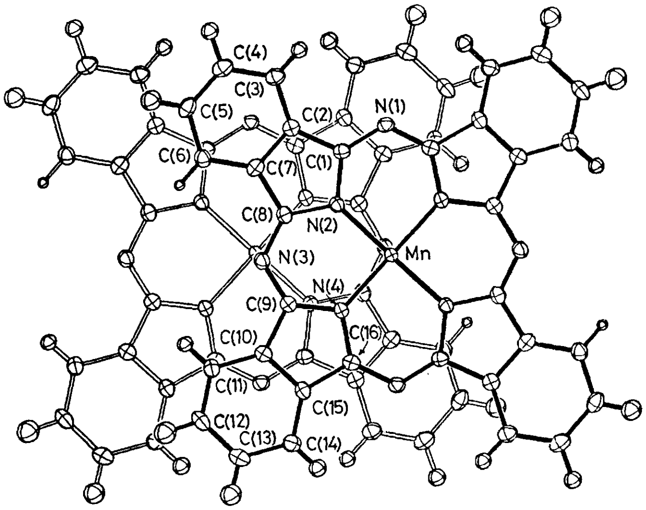

FIGURE 4 An ORTEP drawing of two molecules of [Mn(pc)] (116 K parameters) viewed perpendicular to the N_4 co-ordination planes. The atoms of the shaded molecule are at $(\pm x,\ \pm y,\ \pm z)$, and those of the other molecule are at $(\pm x,\ 1\pm y,\ \pm z)$. Thermal ellipsoids are drawn at the 50% probability level

A view of two molecules perpendicular to the N(4) co-ordination planes (Figure 4) shows the way in which the molecules of [Mn(pc)] and [Co(pc)] pack to give a close M $\cdots$ N(3''),N(3''') contact. However, this packing arrangement also leads to many close contacts between the atoms N(1),N(1') and the pyrrole and benzene residues of adjacent molecules (Table 6). In [Mn(pc)] and [Co(pc)] there are a considerable number of non-bonded intermolecular carbon–carbon and carbon–nitrogen distances between 3.22 and 3.50 Å (the van der Waals radius of N is 1.5 Å and the half-thickness of the aromatic nucleus is [21] 1.70 Å). Strain introduced by these close contacts has been lessened by small but significant deviations of the phthalocyaninate ligand from planarity. The equations of the planes [14] through the central MN_4 atoms of [Mn(pc)] and [Co(pc)] are given in Table 11, together with deviations of other atoms from these planes. It is evident that in each compound the atom N(3) deviates slightly from the plane in the direction of the metal atom with which it interacts. However, the benzene rings in particular are slightly but significantly displaced from the MN_4 plane in the direction away from the adjacent molecule to which they have close contacts; this can be seen by reference to Figure 4 to have the effect of lessening the intermolecular contacts. Not surprisingly, the displacements of the benzene rings from the MN_4 plane are greater in [Mn(pc)], which has the shorter intermolecular contacts, than in [Co(pc)]. It is also evident that the effect of the decrease in temperature of the [Mn(pc)] crystal is to decrease the distance between adjacent molecules related by translations of $\pm b$, and hence to cause a somewhat less planar structure. Each of the benzene and pyrrole residues is essentially planar, and the angles between the various mean planes[14] are given in Table 12 for [Mn(pc)] and [Co(pc)] and for other selected β-polymorph phthalocyanines. It is apparent that all the β-polymorph type structures exhibit a similar pattern of ligand distortions from planarity, to a greater or lesser extent, and that the phthalocyaninate ligand is more planar in H_2pc than in any of the other metallophthalocyanines except, perhaps, [Cu(pc)]. This is in agreement with the greater intermolecular separations in H_2pc and [Cu(pc)], as indicated by the axial M · · · N distances (Table 10). These axial contacts, which are probably of importance in stabilising the β-polymorph structure, are presumably of lesser significance in metal-free H_2pc. As previously recognised,[22] large distortions from planarity in the phthalocyaninate and porphinate macrocycles will have an inimical effect on the delocalised π bonding, whereas relatively smaller deviations from planarity similar to those observed in the β-polymorph phthalocyanines listed in Table 12 probably have a negligible effect on the delocalisation of the π bonding. Much larger deviations of the phthalocyanine macrocycle from planarity are observed in a number of complexes in which the metal atom is significantly displaced from the plane of the four co-ordinating nitrogen atoms of the phthalocyanine ligand. Examples of such non-planar structures are provided by phthalocyaninatotin(II),[23] phthalocyaninatolead(II),[24] bis(phthalocyaninato)metal(IV) complexes of uranium,[25] tin,[26] and thorium,[27] phthalocyaninatomagnesium(II)–dipyridine monohydrate,[28] and the n-hexylamine adduct of [Zn(pc)].[29]

TABLE 11

Equations to the central MN_4 planes through the atoms [a] M, N(2), N(4), N(2′), N(4′), where X, Y, and Z are co-ordinates (Å) with X parallel to a, Y parallel to b, and Z perpendicular to a and b

[Mn(pc)] (116 K) $-0.5640X - 0.6708Y + 0.4816Z = 0$
(295 K) $-0.5639X - 0.6730Y + 0.4786Z = 0$
[Co(pc)] (295 K) $-0.5618X - 0.6777Y + 0.4745Z = 0$

Displacements (Å) from MN_4 plane:

	[Mn(pc)]		
Atom	116 K	295 K	[Co(pc)]
M‴ [b]	−3.180	−3.200	−3.234
N(1)	0.012	−0.002	0.009
N(3)	−0.041	−0.041	−0.026
C(1)	0.031	0.030	0.026
C(2)	0.080	0.075	0.063
C(3)	0.166	0.156	0.130
C(4)	0.232	0.213	0.182
C(5)	0.213	0.198	0.166
C(6)	0.120	0.121	0.093
C(7)	0.058	0.048	0.043
C(8)	−0.002	−0.008	−0.001
C(9)	−0.007	−0.011	−0.002
C(10)	0.058	0.057	0.046
C(11)	0.118	0.111	0.091
C(12)	0.208	0.211	0.152
C(13)	0.225	0.216	0.176
C(14)	0.161	0.155	0.126
C(15)	0.080	0.073	0.064
C(16)	0.027	0.022	0.019

[a] Primed atoms are related to the unprimed atoms by the centre of inversion. [b] M‴, related to M by the operation ($-x$, $1 - y$, $-z$), is the metal atom with which N(3) interacts.

By reference to Figure 3, it is evident that there are close contacts, most of which involve hydrogen atoms, between screw-axis related molecules. The most significant of these contacts (Table 6) is N(3) · · · H(3^{I}) {[Mn(pc)] (116 K) 2.63(5); [Co(pc)] 2.62(5) Å}, considering the van der Waals radii of 1.5 and 1.2 Å for N and H respectively,[21] and the fact that the actual contact distance is probably less than the value calculated using refined hydrogen-atom positions. Significantly, the N(3) atom is displaced from the MN_4 plane away from the direction of contact with H(3^{I}) [where superscript I indicates the co-ordinate transformation ($-x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$)].

Among the β-polymorphs [M(pc)] (M = Mn, Fe, Co, Cu, or Zn) and H_2pc, the largest distortions from planarity are found in [Mn(pc)] where the angle between planes of adjacent benzene rings is 6.3°. This degree of non-planarity is quite commonly found in the square-planar metalloporphyrins, which also display markedly larger distortions in several cases due to the complexing within the central cavity of the macrocycle of a metal atom that is of incorrect size, or to packing forces within the crystal, or to a combination of both effects.[22] The normal radius of the cavity in an undistorted metalloporphyrin has been estimated to be 2.01 Å,[30] and it is postulated that 1.96 Å is the smallest radius the cavity can have in an essentially planar compound.[22,30] Examples of a size ' mismatch ' which results in severe non-planarity of a porphyrin-type ligand are found in

TABLE 12

Angles (°) between various mean planes in selected phthalocyanines

Plane (1): M, N(2), N(4), N(2′), N(4′)
Plane (2): N(2), C(1), C(2), C(7), C(8)
Plane (3): N(4), C(9), C(10), C(15), C(16)
Plane (4): C(2), C(3), C(4), C(5), C(6), C(7)
Plane (5): C(10), C(11), C(12), C(13), C(14), C(15)

	[Mn(pc)]			
Planes	116 K	295 K	[Fe(pc)] [11,*]	[Co(pc)]
(1), (2)	2.1	2.0	1.6	1.6
(1), (3)	2.2	2.1	1.6	1.7
(1), (4)	3.8	3.6	2.9	3.1
(1), (5)	3.7	3.7	2.6	2.8
(2), (3)	4.0	3.8	2.9	3.1
(2), (4)	1.8	1.8	1.3	1.5
(2), (5)	5.2	5.2	3.8	4.0
(3), (4)	5.4	5.0	4.0	4.2
(3), (5)	1.6	1.7	1.1	1.1
(4), (5)	6.3	6.0	4.7	5.0

Planes	[Cu(pc)] [17,*]	[Zn(pc)] [18,*]	H_2pc [19,*]
(1), (2)	0.2	1.9	1.4
(1), (3)	1.6	2.5	1.7
(1), (4)	1.7	3.1	2.2
(1), (5)	2.1	3.6	2.0
(2), (3)	1.8	3.6	2.4
(2), (4)	1.5	1.1	0.8
(2), (5)	2.3	4.6	2.7
(3), (4)	2.9	4.5	2.9
(3), (5)	0.5	1.1	0.3
(4), (5)	3.5	5.3	3.1

* Values calculated using reported atomic co-ordinates.

two low-spin square-planar nickel(II) complexes,[31,32] since normal Ni^{II}–N bond lengths in square-planar complexes are *ca.* 1.85 Å,[33] and the porphinate core must be in a contracted state to accommodate the undersized low-spin nickel(II) atom. Metal atom–cavity size ' mismatch ' is a possible source of non-planarity in the phthalocyanines also, and the normal radius of the cavity for minimum strain in the core of a metallophthalocyanine has been estimated to be *ca.* 1.90 Å,[22] significantly shorter than the 2.01 Å radius estimated [30] in the metalloporphyrins. Hence it is not surprising that in dichloro(phthalocyaninato)tin(IV),[34] in which the six-co-ordinate tin atom is coplanar with the four pyrrole nitrogen atoms and the Sn–N bond length is 2.051(3) Å, the macrocyclic phthalocyanine ligand is severely non-planar, and that this non-planarity has been attributed [34] to the strain introduced within the ligand by the co-ordination of the oversized tin(IV) atom in the macrocyclic cavity. However, in [$SnCl_2$(pc)] the unit cell and crystal packing are quite different to those found in the β-polymorph structures of compounds listed in Table 12. Of these metallophthalocyanines with closely related structures, [Zn(pc)] [18] has the largest M–N bond length [1.979(2) Å, Table 8] but does not show significantly larger distortions from planarity than any of the other compounds, and in fact the degree of non-planarity is slightly less in [Zn(pc)] than in [Mn(pc)] (Table 12). The range of M–N bond distances the porphinate ligand can support in metalloporphyrin complexes while still maintaining planarity is estimated as 1.96—2.10 Å.[22] Assuming the phthalocyaninate cavity has a radius *ca.* 0.10 Å smaller than the porphinate cavity,[22] and that both ligands are similarly flexible in the range of metal-atom sizes they can accommodate, the range of M–N bond lengths [1.908(2)—1.979(2) Å] for those metallophthalocyanines listed in Table 12 would suggest that, for these cases, metal-atom size is probably not an important factor in determining the observed deviations from planarity.

With regard to constraints imposed on the size of the metal atom co-ordinated within the phthalocyaninate macrocyclic cavity, it is possible to postulate that the intermediate-spin states of the manganese(II) atom ($S = \frac{3}{2}$) in [Mn(pc)] [8] and of the iron(II) atom ($S = 1$) in [Fe(pc)],[35] and the low-spin state of the cobalt(II) atom ($S = \frac{1}{2}$) in [Co(pc)],[10] are consequences of such constraints. The co-ordination of manganese(II), iron(II), and cobalt(II) atoms in intermediate or low rather than high-spin states, which require the presence of an electron in a $d_{x^2-y^2}$ orbital, results in substantially smaller metal-atom radii in the plane of the macrocycle. Hence the observation of the highly unusual intermediate-spin state of Mn^{II} in [Mn(pc)] is a result of the cavity size and ligand-field strength of the phthalocyaninate ligand. By comparison, the manganese(II) atom when complexed with the tetraphenylporphinate ligand,[36] which has a larger cavity radius than the phthalocyaninate macrocycle, is in the usual (for Mn^{II}) high-spin state ($S = \frac{5}{2}$).

The molecular structures of [Mn(pc)] and [Co(pc)] are at present being refined using neutron-diffraction intensity data obtained at 4.2 K, and these results will be reported elsewhere.

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REFERENCES

[1] J. M. Robertson, *J. Chem. Soc.*, 1935, 615.

[2] J. M. Robertson, *J. Chem. Soc.*, 1936, 1195.

[3] R. P. Linstead and J. M. Robertson, *J. Chem. Soc.*, 1936, 1736.

[4] J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1937, 219.

[5] J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1940, 36.

[6] A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 27.

[7] C. J. Brown, *J. Chem. Soc.* (*A*), 1968, 2494.

[8] C. G. Barraclough, R. L. Martin, S. Mitra, and R. C. Sherwood, *J. Chem. Phys.*, 1970, **53**, 1638.

[9] H. Miyoshi, H. Ohya-nishiguchi, and Y. Deguchi, *Bull. Chem. Soc. Japan*, 1973, **46**, 2724.

[10] R. L. Martin and S. Mitra, *Chem. Phys. Letters*, 1969, **3**, 183.

[11] J. F. Kirner, W. Dow, and W. R. Scheidt, *Inorg. Chem.*, 1976, **15**, 1685.

[12] P. E. Fielding and A. G. MacKay, *Austral. J. Chem.*, 1964, **17**, 750.

[13] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3, p. 162.

[14] J. M. Stewart, ' The *X*-Ray System,' Version of July 1972, Technical Report TR 72–192, the Computer Science Centre, University of Maryland (' *X*-Ray '74 ' version implemented at Atlas Computer Laboratory).

[15] (*a*) D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104; (*b*) D. T. Cromer, *ibid.*, p. 17.

[16] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[17] C. J. Brown, *J. Chem. Soc.* (*A*), 1968, 2488.

[18] W. R. Scheidt and W. Dow, *J. Amer. Chem. Soc.*, 1977, **99**, 1101.

[19] B. F. Hoskins, S. A. Mason, and J. C. B. White, *Chem. Comm.*, 1969, 554; B. F. Hoskins and S. A. Mason, personal communication.

[20] F. Cariati, F. Morazzoni, and M. Zocchi, *Inorg. Chim. Acta*, 1975, **14**, L31.

[21] L. Pauling, ' The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 1960, p. 260.

[22] J. L. Hoard, *Ann. N.Y. Acad. Sci.*, 1973, **206**, 18.

[23] M. K. Friedel, B. F. Hoskins, R. L. Martin, and S. A. Mason, *Chem. Comm.*, 1970, 400.

[24] K. Ukei, *Acta Cryst.*, 1973, **B29**, 2290.

[25] A. Gieren and W. Hoppe, *Chem. Comm.*, 1971, 413.

[26] W. E. Bennett, D. E. Broberg, and N. C. Baenziger, *Inorg. Chem.*, 1973, **12**, 930.

[27] I. S. Kirin, A. B. Kolyadin, and A. A. Lychev, *Zhur. strukt. Khim.*, 1974, **15**, 486.

[28] M. S. Fischer, D. H. Templeton, A. Zalkin, and M. Calvin, *J. Amer. Chem. Soc.*, 1971, **93**, 2622.

[29] T. Kobayashi, T. Ashida, N. Uyeda, E. Suito, and M. Kakudo, *Bull. Chem. Soc. Japan*, 1971, **44**, 2095.

[30] D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, 1970, **92**, 3761.

[31] E. F. Meyer, jun., *Acta Cryst.*, 1972, **B28**, 2162.

[32] D. P. Arnold, R. Gaete-Holmes, A. W. Johnson, A. R. P. Smith, and G. A. Williams, *J.C.S. Perkin I*, 1978, 1660.

[33] L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 199.

[34] D. Rogers and R. S. Osborn, *Chem. Comm.*, 1971, 840.

[35] C. G. Barraclough, R. L. Martin, S. Mitra, and R. C. Sherwood, *J. Chem. Phys.*, 1970, **53**, 1643.

[36] J. F. Kirner, C. A. Reed, and W. R. Scheidt, *J. Amer. Chem. Soc.*, 1977, **99**, 1093.