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The Structure of Phthalocyaninatomanganese(II) at 5·8 K Determined by Neutron Diffraction

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Abstract

The molecular structure of the β-polymorphic form of phthalocyaninatomanganese(II), [Mn(pc)], $(C_{32}H_{16}MnN_8)$ has been determined at 5·8 K by single-crystal neutron diffraction methods. The crystals are monoclinic, space group $P2_1/c$, $a = 14·601$ (5), $b = 4·69$ (1), $c = 19·327$ (5) Å, $\beta = 121·10$ (1)°, $U = 1133·3$ Å³, $Z = 2$. Intensities for 1133 independent $h0l$ and $h1l$ Bragg reflections were measured using an automatic diffractometer. In addition, a number of reflections forbidden by the space group were examined. The structure has been refined by full-matrix least-squares methods to R_F 0·027, R_{F^2} 0·038 and χ 3·24. Bond lengths at 5·8 K show systematic deviations from those determined previously at 295 and 116 K by X-ray diffraction data of moderate resolution. As in the case of phthalocyaninato-cobalt(II), these deviations are ascribed largely to the effects of asphericity of the valence electron density. The intermolecular axial Mn···N contact, of importance in the ferromagnetic exchange path in [Mn(pc)] $(T_c = 8·6$ K), is 3·115 (4) Å at 5·8 K, compared with 3·148 (2) and 3·169 (6) Å at 116 and 295 K respectively. The neutron scattering length of manganese was found by least-squares refinement to be $-3·59$ (8) fm. The data have been examined for any contribution to the Bragg intensities by magnetic scattering from the ferromagnetic crystal. The possibility that the

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goodness-of-fit, χ, for the refinement differs significantly from unity due to such magnetic contributions is discussed.

Introduction

Metallophthalocyanines have received much experimental and theoretical investigation of their geometrical and electronic structures, largely because of their generic relation to the naturally occurring porphyrins, chlorins, and corrins found as chromophores in hæmoglobin, myoglobin, the cytochromes, chlorophylls, and vitamin B_{12}. Our interest in the metallophthalocyanines has been detailed in previous papers (Mason, Williams & Fielding, 1979; Figgis, Kucharski & Williams, 1980; Williams, Figgis, Mason, Mason & Fielding, 1980) which form part of an on-going series of studies aimed at determining the mechanism of metal–ligand bonding in these macrocycles, together with their geometrical and magnetic structures.

The β-polymorphic form of phthalocyaninatomanganese(II), [Mn(pc)], $(Mn^{II}, S = \frac{3}{2})$ which is the subject of the present study, is a rare example of a ferromagnetic molecular crystal, with $T_c = 8·6$ K (Barraclough, Martin, Mitra & Sherwood, 1970; Miyoshi, Ohya-nishiguchi & Deguchi, 1973). This compound also attracts considerable interest as it is an example of the unusual intermediate state, $S = \frac{3}{2}$, for the d^5 configuration. The magnetic susceptibility, magnetic anisotropy and magnetization properties of the compound have been studied in considerable detail (Barraclough et al., 1970; Miyoshi et al., 1973; Miyoshi, 1974; Barraclough, Gregson & Mitra, 1974) over a large temperature range. [Mn(pc)], together with β-phthalocyaninatocobalt(II), [Co(pc)], $(Co^{II}, S = \frac{1}{2})$ which remains a paramagnet at 4·2 K (Martin & Mitra, 1969; Mitra, 1978), have been studied using the technique of polarized neutron diffraction (Figgis, Mason, Smith & Williams, 1979; Williams, Figgis & Mason, 1980; Figgis, Forsyth, Mason & Williams, 1980) to determine the spin-density distributions in these complexes.

The crystal and molecular structure of [Mn(pc)] has been determined at 295 (Mason et al., 1979) and 116 K (Mason et al., 1979; Figgis, Kucharski & Williams, 1980) by single-crystal X-ray diffraction methods. The determination of the structure at 5·8 K by single-crystal neutron diffraction methods, reported below, was undertaken to assist both in the 4·2 K polarized neutron data treatment and in the interpretation of the ensuing spin-density distribution in [Mn(pc)]. These studies will be reported elsewhere (Figgis, Forsyth, Mason & Williams, 1980).

Experimental

Large single crystals of [Mn(pc)] suitable for neutron diffraction studies, grown by entrainer vacuum-

sublimation techniques (Fielding & MacKay, 1964), were made available by Dr P. E. Fielding of the University of New England. Crystal data for the present study, together with those from the 295 and 116 K X-ray diffraction studies, are presented in Table 1. Neutron diffraction intensity data were obtained at 5·8 K on the D15 normal-beam diffractometer 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 × 10⁴ n mm⁻² s⁻¹. The $\lambda/2$ contamination was <0·08%. At the time of the data collection, the lifting counter of the diffractometer had not been motorized for motion perpendicular to the equatorial plane. This required alignment of the b (needle) axis of the crystal with the ω–2θ diffractometer axis, a condition which maximizes multiple-diffraction effects. Unit-cell parameters and their estimated standard deviations (e.s.d.'s) at 5·8 K, with the exception of b, were derived by a least-squares analysis of the setting angles determined for ten reflections well separated in angle. The b cell parameter was determined manually on the diffractometer by centring several $h1l$ and $h2l$ reflections, and an estimate was made of the error in this parameter.

In order to verify the space group at 5·8 K as $P2_1/c$, the systematically absent reflections $h0l$ with l odd were investigated. All these reflections were found to be present with very weak intensities (typically, $F_o^2 \sim 0·54$ on absolute scale). Possible explanations for these 'forbidden' intensities, other than a space-group change, are that they arise from a general background of multiple diffraction, or from magnetic scattering from the ferromagnetically ordered domains of [Mn(pc)]. This latter possibility, discussed in some detail in the Appendix, was suggested by a separate experiment on [Mn(pc)] at 4·2 K using a polarized neutron diffractometer. It was observed that the intensities of several of these 'forbidden' reflections at

Table 1. *Crystal data for* [Mn(pc)], $C_{32}H_{16}MnN_8$

	295 K*	116 K*	5·8 K
M_r	567·49	567·49	567·49
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	14·576 (5)	14·590 (3)	14·601 (5)
b (Å)	4·755 (1)	4·741 (1)	4·69 (1)
c (Å)	19·362 (7)	19·301 (5)	19·327 (5)
β (°)	120·70 (2)	120·79 (1)	121·10 (1)
U (Å³)	1153·9	1146·9	1133·3
Z	2	2	2
D_c (Mg m⁻³)	1·633	1·643	1·663
λ (Å)	0·70926	0·71069	1·175
	(X-ray)	(X-ray)	(neutron)
μ(mm⁻¹)†	0·6490	0·6530	0·0036
Crystal dimensions (mm)‡	0·04 × 0·10 × 0·53	0·04 × 0·10 × 0·53	0·5 × 1·0 × 13·0
Unique data	1525	1608	1133
	$I > 2\sigma(I)$	$I > 3\sigma(I)$	
$(\sin \theta)/\lambda$ limit (Å⁻¹)	0·705	0·662	0·737

* Mason *et al.* (1979).
† *International Tables for X-ray Crystallography* (1968).
‡ The largest dimension in each case coincides with the b axial direction.

low $(\sin \theta)/\lambda$ values increased by a factor of ~ 2 on application of an external magnetic field of $1 \cdot 5$ T to the crystal. However, in the present study integrated intensities for these 'forbidden' data were obtained above the ordering temperature $(T_c = 8 \cdot 6$ K) at 13 K and were of essentially the same magnitude as those measured at $5 \cdot 8$ K. Furthermore, the intensities of the 'forbidden' data did not fall off rapidly with $(\sin \theta)/\lambda$, as does the magnetic form factor. These two observations indicated that at least the major component of the 'forbidden' intensity was not magnetic in origin.

The fact that the average $\bar{F}_o^2$ for the 'forbidden' data in a small $(\sin \theta)/\lambda$ range was, within experimental error, a constant of magnitude $0 \cdot 54$ (on absolute scale) over the $(\sin \theta)/\lambda$ range of the data suggested multiple scattering as the likely source of the intensity. Further proof of this was provided in a later experiment on [Co(pc)] on the same diffractometer (Williams, Figgis, Mason, Mason & Fielding, 1980). In this case, similar 'forbidden' intensities were observed with the crystal b axis aligned with the $\omega-2\theta$ axis of the diffractometer. When the crystal was offset by about $5°$, these intensities in general decreased in magnitude. Finally, as expected in a situation with significant multiple diffraction, none of the 1133 unique allowed reflections measured had a negative integrated intensity (Hirshfeld & Rabinovich, 1973).

Throughout the data collection, the temperature was monitored and remained steady at $5 \cdot 8 \pm 0 \cdot 2$ K. Intensities were measured *via* an $\omega-2\theta$ scan, and the intensities of two standard reflections observed throughout the data collection had standard deviations of $0 \cdot 006$. Integrated intensities were obtained using a profile-analysis program, *COLL5*, (Lehmann & Wilson, 1979) and geometrical corrections were applied. Absorption corrections were not considered necessary, because of the small linear absorption coefficient (Table 1). Equivalent reflections, where measured, were averaged after any observations which were obviously seriously affected by multiple diffraction effects were discarded. For the averaging of 143 pairs of equivalent reflections, the agreement factor A $[= \sum \text{Average}(|F_o^2 - \bar{F}_o^2|)/\sum \bar{F}_o^2]$ was $0 \cdot 0063$, including 19 pairs of non-Friedel equivalences whose A is $0 \cdot 023$. F_o^2 is the square of the structure factor for an individual member of a pair of equivalences having a mean value $\bar{F}_o^2$, and the summations are over all such pairs. The only correction possible for the general background of multiply scattered intensity was the subtraction of an averaged quantity from each F_o^2 value (LePage & Gabe, 1979). From an analysis of the 'forbidden' data, this correction was determined as $0 \cdot 54$ for F_o^2 on absolute scale, constant over the $(\sin \theta)/\lambda$ range of the data. The F_o^2 values were corrected for multiple-diffraction effects in this manner.

The cryostat design on the D15 diffractometer prevented the lifting detector being raised more than

$25°$ above the equatorial plane. Therefore, only the $h0l$ and $h1l$ 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 this hardware limit, and within the range $(\sin \theta)/\lambda < 0 \cdot 737$ Å^{-1}, were measured. Of the 1133 unique reflections observed and used in the refinement, 415 and 718 were of the $h0l$ and $h1l$ types respectively.

Structure refinement

The structure was refined using the least-squares program *CRYLSQ* (Stewart, 1976) in the full-matrix mode, the function minimized being $\sum w(F_o^2 - F_c^2)^2$ where w is the weight assigned to the F_o^2 values. The weight for an individual observation was based on counting statistics $[\sigma(F_o^2)]$, and included also a term in F_o^2 to allow for machine instability and other errors proportional to diffracted intensity, and a constant factor to allow for multiple-scattering effects. The term in F_o^2 was estimated from the average variance of the F_o^2 values of the 19 non-Friedel pairs of equivalences. The constant factor was derived from the variance of the F_o^2 values of the 'forbidden' reflections about their average, giving $w = 1/k^2[\sigma^2(F_o^2) + (0 \cdot 012F_o^2)^2 + 9 \cdot 0]$ where k^2 is a scale factor to place F_o^2 on absolute scale. All 1133 observations, including the negative F_o^2 values (Hirshfeld & Rabinovich, 1973) which arose after the multiple-scattering correction, were used in the refinement. Starting parameters were obtained from the $4 \cdot 3$ K structure of [Co(pc)] (Williams, Figgis, Mason, Mason & Fielding, 1980). All atoms were assigned isotropic thermal parameters, and in initial refinement cycles the y coordinate of each atom was held invariant. Upon inclusion of the y coordinates in the refinement, no unexpectedly large shifts were observed so refinement continued using all positional parameters as variables. The anisotropic thermal parameters of the H atoms were refined in two dimensions only, with U_{11}, U_{33}, and U_{13} as variables, U_{22} fixed with the value of the refined isotropic temperature factor, and U_{12} and U_{23} fixed at zero. An examination of the observed and calculated F^2 values revealed no evidence of any secondary-extinction effects, except in the cases of the three most intense reflections which were given very low weights in the refinement cycles. The scattering length of Mn was also included in the final refinement cycles (131 variables). Refinement converged with R_{F^2} $(= \sum |F_o^2 - F_c^2|/\sum F_o^2)$ $0 \cdot 038$, R_F $(= \sum ||F_o| - |F_c||/\sum |F_o|)$ $0 \cdot 027$ and a goodness-of-fit index, χ $\{= [\sum w(F_o^2 - F_c^2)^2/(1133 - 131)]^{1/2}\}$, of $3 \cdot 24$. The maximum parameter shift-to-error ratio at convergence was $0 \cdot 04:1$. A final difference Fourier synthesis was featureless. The neutron scattering length of Mn refined to $-3 \cdot 59$ (8) fm, with the scattering

Table 2. Details of refinements employing different portions of the data

R_F, R_{F^2} and χ are defined in the text. $R_F' = [\sum w(|F_o| - |F_c|)^2/ \sum w|F_o|^2]^{1/2}$. All refinements went to convergence.

	All 1133 reflections with $(\sin\theta)/\lambda \leq$ 0·737 Å^{-1}	948 reflections with 0·3 $\leq$ $(\sin\theta)/\lambda \leq$ 0·737 Å^{-1}	773 reflections with $k + l$ even	360 reflections with $k + l$ odd
R_F	0·027	0·023	0·025	0·024
R_F'	0·060	0·052	0·055	0·059
R_{F^2}	0·038	0·032	0·038	0·032
χ	3·24	2·16	3·08	2·94
Number of variables	131	130^a	130^a	77^{a,b}

(a) The scattering length of Mn was fixed at the value from the refinement employing all data.
(b) The y coordinates of all atoms, and isotropic and anisotropic thermal parameters of Mn and H atoms respectively, were invariant and given their refined values as in (a).

Table 3. Final atomic positional and thermal parameters for [Mn(pc)] at 5·8 K

The e.s.d.'s (in parentheses) are those obtained in the usual manner from the least-squares refinement. U tensors are in Å^2 ($\times 10^4$). 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 $T = \exp[-8\pi^2U_{iso}(\sin^2\theta)/\lambda^2]$ respectively. H atoms were refined anisotropically in two dimensions (xz plane) only; the U_{22} parameters were held invariant at the values obtained from the isotropic refinement, and U_{12} and U_{23} were set to 0·0 in each case. The isotropic thermal parameters for H atoms are presented here, and anisotropic values have been deposited.

	x	y	z	U_{iso}
Mn	0	0	0	19 (10)
N(1)	0·25379 (7)	0·0312 (7)	0·16211 (5)	48 (2)
N(2)	0·07392 (7)	0·2248 (7)	0·09808 (5)	47 (2)
N(3)	−0·07190 (7)	0·5371 (7)	0·07777 (5)	52 (2)
N(4)	−0·13291 (7)	0·2000 (7)	−0·03395 (5)	46 (2)
C(1)	0·1806 (1)	0·2013 (11)	0·1596 (1)	41 (2)
C(2)	0·2018 (1)	0·4023 (11)	0·2233 (1)	44 (2)
C(3)	0·2933 (1)	0·4574 (11)	0·2984 (1)	55 (2)
C(4)	0·2851 (1)	0·6685 (11)	0·3467 (1)	57 (2)
C(5)	0·1887 (1)	0·8185 (11)	0·3209 (1)	56 (2)
C(6)	0·0981 (1)	0·7636 (11)	0·2462 (1)	52 (2)
C(7)	0·1063 (1)	0·5534 (11)	0·1979 (1)	42 (2)
C(8)	0·0280 (1)	0·4412 (11)	0·1194 (1)	41 (2)
C(9)	−0·1458 (1)	0·4213 (11)	0·0087 (1)	42 (2)
C(10)	−0·2567 (1)	0·5095 (11)	−0·0334 (1)	46 (2)
C(11)	−0·3103 (1)	0·7101 (11)	−0·0141 (1)	60 (2)
C(12)	−0·4201 (1)	0·7386 (11)	−0·0673 (1)	69 (2)
C(13)	−0·4745 (1)	0·5719 (11)	−0·1379 (1)	65 (2)
C(14)	−0·4207 (1)	0·3701 (11)	−0·1570 (1)	56 (2)
C(15)	−0·3105 (1)	0·3405 (11)	−0·1035 (1)	43 (2)
C(16)	−0·2316 (1)	0·1521 (11)	−0·1033 (1)	41 (2)
H(1)	0·3676 (2)	0·3545 (24)	0·3180 (2)	201 (7)
H(2)	0·3543 (2)	0·7101 (24)	0·4057 (2)	186 (7)
H(3)	0·1853 (3)	0·9672 (25)	0·3604 (2)	205 (7)
H(4)	0·0229 (2)	0·8715 (24)	0·2255 (2)	200 (7)
H(5)	−0·2675 (2)	0·8434 (25)	0·0400 (2)	202 (7)
H(6)	−0·4643 (2)	0·8932 (25)	−0·0548 (2)	218 (7)
H(7)	−0·5604 (2)	0·6037 (24)	−0·1788 (2)	194 (7)
H(8)	−0·4628 (2)	0·2434 (24)	−0·2113 (2)	196 (7)

lengths for C, H, and N taken from *International Tables for X-ray Crystallography* (1974).

To check the possibility of the contributions of magnetic scattering to the intensity data, separate refinements were then carried out on portions of the data to which the magnetic contribution would be expected to differ. The results of these refinements are presented in Table 2, and discussed in the Appendix.

Final atomic positional and thermal parameters from the refinement on all the data are listed in Table 3. All computations were performed on a Perkin Elmer 8/32 computer at the Crystallography Centre of The University of Western Australia.*

Discussion

The molecular geometry of the centrosymmetric [Mn(pc)] molecule at 5·8 K and the numbering scheme are shown in Fig. 1. Interatomic distances, angles and correlated e.s.d.'s† are given in Tables 4, 5 and 6. The corresponding intramolecular distances obtained from 116 and 295 K X-ray diffraction data (Mason *et al.*, 1979; Figgis, Kucharski & Williams, 1980) are presented in Table 4 for comparison. The interatomic distances and angles presented in the tables are obtained from the atomic parameters in Table 3, from the refinement employing all the data. Although the goodness-of-fit for these data was quite high (Table 2), perhaps due to a magnetic contribution to the inten-

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* Lists of structure factors and anisotropic thermal parameters for the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35516 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

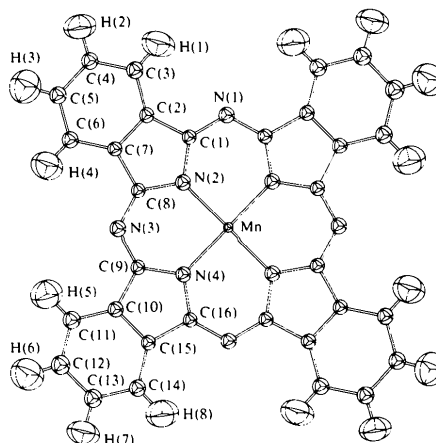† The e.s.d.'s contain contributions from the e.s.d.'s in the cell parameters.

Fig. 1. An *ORTEP* drawing (Johnson, 1965) of [Mn(pc)] (5·8 K parameters) showing the molecular geometry and atom numbering. The thermal ellipsoids are drawn at the 99% probability level.

Table 4. *Interatomic distances* (Å) *in* [Mn(pc)]

	5·8 K neutron refinement	Level I 116 K[b] X-ray refinement	Level II 116 K[c] X-ray refinement	295 K[d] X-ray refinement
Intramolecular distances[a]				
Mn—N(2)	1·938 (2)	1·936 (2)	1·940 (2)	1·933 (4)
Mn—N(4)	1·939 (2)	1·940 (2)	1·944 (2)	1·933 (5)
N(1)—C(1)	1·315 (4)	1·319 (4)	1·329 (3)	1·315 (9)
N(1)—C(16')	1·324 (4)	1·314 (4)	1·319 (3)	1·308 (8)
N(2)—C(1)	1·392 (1)	1·402 (3)	1·394 (2)	1·403 (6)
N(2)—C(8)	1·391 (5)	1·383 (4)	1·381 (3)	1·382 (9)
N(3)—C(8)	1·328 (3)	1·327 (3)	1·331 (3)	1·330 (7)
N(3)—C(9)	1·325 (3)	1·328 (3)	1·329 (2)	1·312 (6)
N(4)—C(9)	1·397 (5)	1·381 (4)	1·381 (3)	1·391 (8)
N(4)—C(16)	1·389 (2)	1·399 (3)	1·391 (2)	1·399 (6)
C(1)—C(2)	1·451 (5)	1·451 (4)	1·449 (3)	1·446 (9)
C(2)—C(3)	1·397 (2)	1·398 (3)	1·403 (3)	1·397 (7)
C(2)—C(7)	1·408 (4)	1·394 (4)	1·396 (3)	1·383 (8)
C(3)—C(4)	1·408 (5)	1·377 (5)	1·391 (4)	1·369 (11)
C(4)—C(5)	1·414 (4)	1·393 (4)	1·403 (4)	1·391 (10)
C(5)—C(6)	1·389 (2)	1·381 (3)	1·392 (3)	1·378 (7)
C(6)—C(7)	1·404 (5)	1·393 (4)	1·401 (4)	1·398 (10)
C(7)—C(8)	1·447 (3)	1·443 (3)	1·441 (3)	1·432 (7)
C(9)—C(10)	1·448 (3)	1·446 (3)	1·445 (3)	1·447 (7)
C(10)—C(11)	1·392 (5)	1·385 (5)	1·397 (4)	1·408 (11)
C(10)—C(15)	1·407 (4)	1·395 (3)	1·398 (3)	1·386 (8)
C(11)—C(12)	1·393 (2)	1·390 (4)	1·396 (3)	1·383 (8)
C(12)—C(13)	1·410 (4)	1·387 (4)	1·400 (4)	1·386 (10)
C(13)—C(14)	1·396 (5)	1·382 (5)	1·393 (4)	1·384 (11)
C(14)—C(15)	1·399 (2)	1·394 (3)	1·399 (3)	1·382 (7)
C(15)—C(16)	1·452 (5)	1·453 (4)	1·453 (4)	1·447 (9)
H(1)—C(3)	1·063 (6)	0·95 (3)	1·00 (2)	0·90 (7)
H(2)—C(4)	1·082 (3)	1·03 (2)	1·04 (2)	0·99 (4)
H(3)—C(5)	1·053 (9)	0·96 (3)	0·99 (3)	0·84 (7)
H(4)—C(6)	1·080 (7)	0·97 (2)	0·99 (2)	0·97 (7)
H(5)—C(11)	1·096 (8)	0·92 (2)	0·97 (2)	0·92 (5)
H(6)—C(12)	1·078 (9)	0·98 (3)	1·02 (3)	0·83 (10)
H(7)—C(13)	1·093 (3)	1·00 (2)	1·00 (2)	0·98 (6)
H(8)—C(14)	1·079 (7)	0·94 (2)	0·95 (2)	0·95 (6)
Mn···N(1)	3·402 (1)	3·399 (2)	3·407 (2)	3·392 (4)
Mn···N(3)	3·367 (3)	3·358 (3)	3·364 (2)	3·352 (6)
N(2)···N(4)	2·772 (1)	2·761 (2)	2·769 (2)	2·757 (5)
N(2)···N(4')	2·711 (5)	2·721 (3)	2·723 (3)	2·710 (8)

Selected intermolecular contacts perpendicular to molecular plane

Mn···N(3")	3·115 (4)	3·148 (3)	3·148 (2)	3·169 (6)
Mn···C(8")	3·374 (6)	3·409 (3)	3·409 (2)	3·427 (6)
Mn···C(9")	3·506 (6)	3·545 (3)	3·543 (2)	3·554 (6)

(a) Primed and double-primed atoms are related to the unprimed atom by the operations (−x,−y,−z) and (x, −1 + y, z) respectively.
(b) 116 K X-ray refinement using all 2265 measured Bragg intensities with (sin θ)/$\lambda \leq 0.662$ Å^{-1} (Figgis, Kucharski & Williams, 1980).
(c) Refinement as in (b) but including allowance for aspherical valence density in the scattering model (Figgis, Kucharski & Williams, 1980).
(d) 295 K X-ray data refinement using 1525 observed [$I > 2\sigma(I)$] data with (sin θ)/$\lambda \leq 0.705$ Å^{-1} (Mason et al., 1979).

Table 5. *Intermolecular contacts* (Å) *in* [Mn(pc)] *at* 5·8 K

Contacts perpendicular to molecular plane*†

Mn···N(3")	3·115 (4)	C(1)···C(10''')	3·438 (4)
Mn···C(8")	3·374 (6)	C(1)···C(15''')	3·395 (6)
Mn···C(9")	3·506 (6)	C(1)···C(16''')	3·431 (8)
N(1)···C(2")	3·407 (8)	C(2)···C(5")	3·386 (8)
N(1)···C(7")	3·417 (5)	C(2)···C(6")	3·486 (8)
N(1)···C(10''')	3·307 (5)	C(2)···C(16''')	3·313 (6)
N(1)···C(15''')	3·409 (8)	C(3)···C(5")	3·491 (8)
N(2)···C(6")	3·457 (5)	C(7)···C(16''')	3·471 (4)
N(2)···N(4''')	3·265 (6)	C(14)···C(12")	3·430 (8)
N(2)···C(9''')	3·216 (4)	C(15)···C(11")	3·423 (8)
N(4)···C(8")	3·243 (4)	C(15)···C(12")	3·488 (8)
C(1)···C(6")	3·248 (6)	C(16)···C(10")	3·399 (8)
C(1)···C(7")	3·433 (9)	C(16)···C(11")	3·262 (6)
C(1)···C(9''')	3·501 (4)		

Other intermolecular contacts†‡

N(3)···H(3$^{\mathrm{I}}$)	2·515 (5)	C(4)···H(7$^{\mathrm{II}}$)	2·761 (6)
N(3)···C(5$^{\mathrm{I}}$)	3·352 (3)	H(2)···H(6$^{\mathrm{II}}$)	2·396 (6)
C(4)···H(5$^{\mathrm{I}}$)	2·787 (8)	N(1)···H(7$^{\mathrm{III}}$)	2·932 (4)
C(6)···H(4$^{\mathrm{I}}$)	2·794 (9)	H(1)···C(13$^{\mathrm{III}}$)	2·830 (10)
C(9)···H(3$^{\mathrm{I}}$)	2·881 (5)	H(1)···C(14$^{\mathrm{III}}$)	3·059 (6)
C(10)···H(3$^{\mathrm{I}}$)	2·951 (4)	H(1)···H(7$^{\mathrm{III}}$)	2·380 (15)
C(11)···H(3$^{\mathrm{I}}$)	2·803 (6)	C(13)···H(8$^{\mathrm{IV}}$)	2·687 (5)
H(5)···H(3$^{\mathrm{I}}$)	2·424 (12)	C(14)···H(8$^{\mathrm{IV}}$)	2·822 (8)
C(3)···H(7$^{\mathrm{II}}$)	2·833 (10)	H(7)···H(8$^{\mathrm{IV}}$)	2·408 (7)

* Double-primed and triple-primed atoms are related by the coordinate transformations $(x, -1 + y, z)$ and $(-x, 1 - y, -z)$ respectively.
† All unique intermolecular contacts are given within the limits of the contact radii: Mn, 2·1; N, C, 1·75; H, 1·25 Å.
‡ Roman-numeral superscripts refer to the following coordinate 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) $-1 - x, \frac{1}{2} + y, -\frac{1}{2} - z$.

sities of low (sin θ)/λ data as discussed in the Appendix, the atomic positions obtained from the refinements employing only portions of the data set did not vary significantly from those obtained using the full set.

Bond distances from the neutron analysis show significant systematic differences from those obtained from the X-ray studies using data of only moderate resolution. Similar systematic deviations were evident in the neutron and X-ray diffraction analyses of [Co(pc)] (Williams, Figgis, Mason, Mason & Fielding, 1980) and were discussed in terms of the asymmetrical distribution of valence electron density about atoms in asymmetrical environments. The neutron diffraction method yields the true nuclear positions, whereas refinements based on X-ray diffraction data give the atomic position at the centroid of the electron density. For first-row atoms in particular, in asymmetrical environments, with X-ray data of only moderate resolution the apparent centroid of the electronic charge does not coincide with the nuclear position (Coppens, 1974). This effect is undoubtedly the major cause of the systematic differences between the neutron- and X-ray-derived bond lengths in [Mn(pc)] (Table 4).

The effects of thermal vibrations on the 295 K bond lengths have been shown to be small in [Co(pc)] (Williams, Figgis, Mason, Mason & Fielding, 1980) in comparison with the size of the deviations between neutron- and X-ray-derived bond lengths actually observed in [Mn(pc)] and [Co(pc)]. The benzene ring C—C distances are particularly sensitive to the apparent bond-shortening effect of moderate resolution X-ray data (Williams, Figgis, Mason, Mason & Fielding, 1980; O'Connell, Rae & Maslen, 1966) and

Table 6. *Bond angles* (°) *in* [Mn(pc)] *at* 5·8 K

Primed and triple-primed atoms are related to the unprimed atom by the operations $(-x,-y,-z)$ and $(-x, 1 - y, -z)$ respectively.

N(2)–Mn–N(4)	91·28 (11)	C(11)–C(10)–C(15)	121·8 (2)
N(2)–Mn–N(4')	88·72 (11)	C(10)–C(11)–C(12)	117·3 (3)
C(1)–N(1)–C(16')	121·9 (1)	C(11)–C(12)–C(13)	121·3 (3)
Mn–N(2)–C(1)	127·2 (2)	C(12)–C(13)–C(14)	121·3 (2)
Mn–N(2)–C(8)	125·2 (1)	C(13)–C(14)–C(15)	117·4 (3)
C(1)–N(2)–C(8)	107·6 (2)	C(10)–C(15)–C(14)	120·9 (3)
C(8)–N(3)–C(9)	122·6 (3)	C(10)–C(15)–C(16)	107·0 (2)
Mn–N(4)–C(9)	125·1 (1)	C(14)–C(15)–C(16)	132·1 (3)
Mn–N(4)–C(16)	127·3 (2)	N(4)–C(16)–C(15)	109·3 (3)
C(9)–N(4)–C(16)	107·5 (2)	N(4)–C(16)–N(1')	127·3 (3)
N(1)–C(1)–N(2)	127·5 (3)	C(15)–C(16)–N(1')	123·4 (1)
N(1)–C(1)–C(2)	123·3 (1)	C(2)–C(3)–H(1)	122·6 (5)
N(2)–C(1)–C(2)	109·2 (3)	C(4)–C(3)–H(1)	120·2 (4)
C(1)–C(2)–C(3)	132·2 (3)	C(3)–C(4)–H(2)	118·3 (5)
C(1)–C(2)–C(7)	106·9 (2)	C(5)–C(4)–H(2)	119·9 (5)
C(3)–C(2)–C(7)	120·8 (3)	C(4)–C(5)–H(3)	119·0 (2)
C(2)–C(3)–C(4)	117·1 (3)	C(6)–C(5)–H(3)	120·1 (3)
C(3)–C(4)–C(5)	121·8 (2)	C(5)–C(6)–H(4)	122·5 (5)
C(4)–C(5)–C(6)	120·9 (3)	C(7)–C(6)–H(4)	120·1 (4)
C(5)–C(6)–C(7)	117·4 (3)	C(10)–C(11)–H(5)	121·3 (3)
C(2)–C(7)–C(6)	122·0 (2)	C(12)–C(11)–H(5)	121·3 (5)
C(2)–C(7)–C(8)	106·7 (3)	C(11)–C(12)–H(6)	119·6 (4)
C(6)–C(7)–C(8)	131·3 (2)	C(13)–C(12)–H(6)	119·1 (3)
N(2)–C(8)–N(3)	128·0 (2)	C(12)–C(13)–H(7)	119·2 (6)
N(2)–C(8)–C(7)	109·6 (2)	C(14)–C(13)–H(7)	119·6 (5)
N(3)–C(8)–C(7)	122·5 (3)	C(13)–C(14)–H(8)	120·9 (3)
N(3)–C(9)–N(4)	127·7 (2)	C(15)–C(14)–H(8)	121·6 (5)
N(3)–C(9)–C(10)	122·8 (3)	N(2)–Mn···N(3''')	86·4 (1)
N(4)–C(9)–C(10)	109·5 (2)	N(4)–Mn···N(3''')	91·6 (1)
C(9)–C(10)–C(11)	131·5 (2)	C(8)–N(3)···Mn'''	89·4 (2)
C(9)–C(10)–C(15)	106·7 (3)	C(9)–N(3)···Mn'''	95·8 (2)

Table 7. *Weighted mean values, together with their estimated standard deviations, of the* 12 *individual benzene-ring* C—C *bond distances in* [Mn(pc)] *and* [Co(pc)]

Refinement	Mean C—C distance (Å)
[Mn(pc)] 5·8 K neutron refinement	1·398 (2)
[Mn(pc)] 116 K X-ray Level I refinement with all 2265 Bragg intensities measured with $(\sin \theta)/\lambda \le 0.662$ Å^{-1}[*]	1·390 (2)
[Mn(pc)] 116 K X-ray Level II refinement including allowance for aspherical valence density in the scattering model[*]	1·397 (1)
[Mn(pc)] 295 K X-ray refinement employing 1525 data with $I > 2\sigma(I)$ and $(\sin \theta)/\lambda \le 0.705$ Å^{-1}[†]	1·386 (3)
[Co(pc)] 4·3 K neutron refinement[‡]	1·395 (1)
[Co(pc)] 295 K X-ray refinement employing 1930 data with $I > 3\sigma(I)$ and $(\sin \theta)/\lambda \le 0.705$ Å^{-1}[†]	1·383 (1)
[Co(pc)] 295 K X-ray refinement as above, bond distances corrected for thermal motion effects[‡]	1·386 (1)

* Figgis, Kucharski & Williams (1980).
† Mason *et al.* (1979).
‡ Williams, Figgis, Mason, Mason & Fielding (1980).

mean values from the various refinements of [Mn(pc)] and [Co(pc)] are presented in Table 7. In both cases, the mean neutron diffraction distance is larger than the X-ray-derived distances. The effect of thermal motion in [Co(pc)] at 295 K is seen to be an apparent shortening of each C—C bond by *ca* 0·003 Å. In the case of [Mn(pc)], the 116 K X-ray refinement yields a mean C—C distance [1·390 (2) Å] closer to the neutron-derived values than the 295 K refinements of both compounds. This is probably due to the smaller effects of thermal vibration at the lower temperature, together with perhaps somewhat better resolution of the core electron density due to the inclusion of all measured data (including negative intensities) in the refinement. The allowance for aspherical valence density effects in this 116 K refinement, by the inclusion of small spherical 'blobs' of charge in the overlap regions between the bonded C atoms (Figgis, Kucharski & Williams, 1980), is seen to yield a mean C—C bond distance essentially in agreement with the neutron-derived values. While in general the bond distances from this latter refinement are in improved agreement with the neutron values, this is not the case with the Mn—N bond lengths (Table 4), which do not appear to be affected by any asymmetry in the electron density about the N atoms.

As discussed for [Co(pc)] (Williams, Figgis, Mason, Mason & Fielding, 1980), the atomic positions ob-

tained from the neutron diffraction method, unlike the X-ray case, are not affected significantly by the fact that the data are of only moderate resolution. However, 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, or for errors arising from any magnetic contribution to the intensities (Appendix), in the e.s.d.'s quoted in the tables. Despite these limitations, the structural parameters from the present neutron study are believed to specify the [Mn(pc)] molecule more accurately than has been done before. Of particular interest is the Mn···N(3'') intermolecular contact. This separation plays a central role in the proposed pathways for the superexchange interaction which leads to the low-temperature ferromagnetism of the compound. At 5·8 K, this contact is considerably shorter [3·115 (4) Å] than at higher temperatures (Table 4) and is the shortest such contact observed in the metallophthalocyanines (Mason *et al.*, 1979; Williams, Figgis, Mason, Mason & Fielding, 1980). The corresponding contact distance in paramagnetic [Co(pc)] at 4·3 K is 3·154 (3) Å (Williams, Figgis, Mason, Mason & Fielding, 1980). Some displacements from and equations of selected mean planes are presented in Tables 8 and 9. A comparison of the atomic displacements from the MnN$_4$ coordination plane at 5·8 K (Table 8) and 116 (Figgis, Kucharski & Williams, 1980) or 295 K (Mason *et al.*, 1979) indicates that a significant source of the decrease in the

Table 8. *Equation to the central* MnN_4 *plane in* [Mn(pc)] *at* 5·8 K *through the atoms* Mn, N(2), N(4), N(2'), N(4'), *where* X, Y, *and* Z *are coordinates* (Å) *with* X *parallel to* **a**, Y *parallel to* **b**, *and* Z *perpendicular to* **a** *and* **b**, *and atomic displacements*

Prime, double- and triple-prime superscripts refer to atoms related to the unprimed atom by the operations $(-x, -y, -z)$, $(x, -1 + y, z)$, and $(-x, 1 - y, -z)$ respectively. The angle between the b axis and the normal to the MnN_4 coordination plane is 47·40°. The angle of the $Mn \cdots N(3'')$, $N(3''')$ contact to the normal of the MnN_4 plane is 3·93°. Mn''' is the manganese atom with which N(3) interacts.

Equation of plane

$$-0.5628X - 0.6769Y + 0.4744Z = 0$$

Displacements from plane (Å)

Mn'''	−3·175 (1)	C(8)	−0·023 (4)
N(1)	−0·001 (3)	C(9)	−0·023 (4)
N(3)	−0·067 (3)	C(10)	0·042 (4)
C(1)	0·027 (4)	C(11)	0·106 (4)
C(2)	0·072 (4)	C(12)	0·201 (4)
C(3)	0·157 (4)	C(13)	0·226 (4)
C(4)	0·204 (4)	C(14)	0·168 (4)
C(5)	0·174 (4)	C(15)	0·078 (4)
C(6)	0·086 (4)	C(16)	0·029 (4)
C(7)	0·035 (4)		

Table 9. *Equations of various mean planes in* [Mn(pc)] *at* 5·8 K

Plane (1): Mn, N(2), N(4), N(2'), N(4') ($\chi^2 = 0.0$)
Plane (2): N(2), C(1), C(2), C(7), C(8) ($\chi^2 = 25.51$)
Plane (3): N(4), C(9), C(10), C(15), C(16) ($\chi^2 = 30.65$)
Plane (4): C(2), C(3), C(4), C(5), C(6), C(7) ($\chi^2 = 0.61$)
Plane (5): C(10), C(11), C(12), C(13), C(14), C(15) ($\chi^2 = 1.47$)

Equations to the least-squares planes (axes defined as in Table 8)

Plane (2): $-0.5827X - 0.6806Y + 0.4440Z = -0.0670$
Plane (3): $-0.5355X - 0.6788Y + 0.5024Z = -0.0741$
Plane (4): $-0.5840X - 0.6953Y + 0.4189Z = -0.1841$
Plane (5): $-0.5072X - 0.6956Y + 0.5088Z = -0.2090$

The angles between plane (1) and planes (2), (3), (4) and (5) are 2·1, 2·2, 3·6 and 3·9° respectively.

$Mn \cdots N(3'')$ contact at very low temperature (interestingly, below the Curie temperature) is the larger deviation {−0·067, −0·044 and −0·041 Å at 5·8, 116, and 295 K respectively in [Mn(pc)] (Mason *et al.*, 1979; Figgis, Kucharski & Williams, 1980), −0·059 and −0·026 Å at 4·3 and 295 K respectively in [Co(pc)] (Williams, Figgis, Mason, Mason & Fielding, 1980)} of the N(3) atom from the MnN_4 coordination plane at low temperature. The angle of the $Mn \cdots N(3'')$ contact to the normal of the MnN_4 coordination plane at 5·8 K (3·93°) is less than at 116 K (4·64°) (Figgis, Kucharski & Williams, 1980), indicating a closer approach to a pseudo-octahedral manganese environment at the low temperature.

APPENDIX
Investigation of magnetic-scattering contributions to the Bragg intensities

As [Mn(pc)] is a ferromagnet at the temperature (5·8 K) of the diffraction experiment, it is possible that magnetic scattering could contribute to the diffracted intensities of the reflections. The total scattering expected is (Tofield, 1975)

$$F_o^2 = F_N^2 + F_M^2$$

where F_N^2 and F_M^2 are the scattering terms due to the nuclei and the magnetization of the crystal respectively. We may write this expression in the form

$$F_o^2 = \alpha \sum_i \left(\sum_j g_j^2 b_j^2 t_j^2 + \sum_{k=1}^{4} p_{Mn}^2 \eta_k^2 t_{Mn}^2 \right)$$

where α is a scale factor for the data; g_j is the structure factor for the jth scattering nucleus; b_j is the scattering length for the jth scattering nucleus; t_j is the temperature factor for the jth scattering nucleus; p_{Mn} is the magnetic scattering length of the Mn atom and equals $(g/2)\langle s \rangle (e^2 \gamma_N / 2mc^2) f(\kappa) \simeq 11 \times 0.27 \times 10^{-12} f(\kappa)$, with g the gyromagnetic ratio for the electronic spin, $\langle s \rangle$, of the Mn atom and $f(\kappa)$ the magnetic form factor for the manganese d electrons. η_k is an orientation factor between the spin vector of the kth domain of the crystal and the scattering vector; and the summation is over the i equivalent positions in the unit cell.

For a crystal composed of a random orientation of domains, $\eta = 0$. However, an account of the magnetization properties of [Mn(pc)] at 4·2 K has been given in terms of a four-domain structure in which the domain spin is directed either along or perpendicular to the b crystal axis (Miyoshi, 1974). In such a model η does not average to zero. In the presence of the nuclear scattering from all the atoms in the molecule, the magnetic contribution from the Mn atom alone is likely to be only minor, although it has been shown to be very important in certain more simple compounds (Tofield, 1975). There remains the possibility that important magnetic contributions could occur for certain reflec-

tions for which F_N is by chance small. Also, the observation of the magnetic-field dependence of the intensities of several of the forbidden reflections of [Mn(pc)], discussed in the text above, led us to query whether the magnetic space group of the compound is indeed the same as that of the nuclear positions. It was to investigate the possibility of magnetic-scattering contributions that measurements of the intensities of a number of forbidden reflections were carried out.

Although the intensities observed for the forbidden reflections indicated no obvious contribution from magnetic scattering, but could be ascribed to multiple-diffraction effects as discussed in the text above, the allowed reflections were examined for magnetic contributions. A *spherically symmetrical* scatterer (manganese) at (0,0,0) in the unit cell of space group $P2_1/c$ does not contribute to the diffracted intensities of hkl reflections of the type $k + l = 2n + 1$. Consequently, these data will not be affected to first order by magnetic-scattering contributions. This is because the magnetization of the unit cell is known to lie mainly on the Mn atoms and the aspherical components of d-electron magnetization are small.

With these considerations in mind, we performed separate refinements of the structure employing (a) the complete data set (1133 observations) as set out in the body of the paper, (b) the $k + l = 2n + 1$ data only (360 observations), and (c) the $k + l = 2n$ data only (773 observations). The details of these refinements are given in Table 2. They provide no clear evidence for any magnetic contributions to the Bragg intensities. A further refinement employing only data with $0·3 \leq$ $(\sin \theta)/\lambda \leq 0·737$ Å^{-1} (Table 2) yielded a model which fits that portion of the data better (χ closer to unity) than the model from (a) fits the complete data set. Therefore, the systematic errors remaining in the data, indicated by $\chi \neq 1$, affect the data at low $(\sin \theta)/\lambda$ values to a greater extent. It is possible that a magnetic contribution to the intensities is the source of such systematic errors, but at this stage, with no firm model of the magnetic ordering available, we cannot treat the effects quantitatively.

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