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The Crystal and Molecular Structure of Phthalocyanatopyridinemanganese(III)-μ-oxo-phthalocyanatopyridinemanganese(III) Dipyridinate

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Received March 13, 1967

The crystal and molecular structure of phthalocyanatopyridinemanganese(III)-μ-oxo-phthalocyanatopyridinemanganese(III) dipyridinate has been determined from an X-ray diffraction study of a single-crystal specimen. Four formula units are contained in an orthorhombic unit cell with $a = 22.635 \pm 0.005$, $b = 23.850 \pm 0.005$, and $c = 12.808 \pm 0.003$ A. The space group is $P2_12_12_1$. The 107 nonhydrogen atoms in the asymmetric unit were refined by least-squares methods using the data from 3156 independent reflections. This novel molecule consists of two approximately flat and parallel manganese phthalocyanine ring systems, joined by an oxygen atom which is midway between the manganese atoms. Each manganese also has a pyridine molecule coordinated opposite to its oxygen atom. The crystals consist of these complex molecules and molecules of pyridine of crystallization.

Introduction

The chemistry of phthalocyanine complexes of manganese are of interest because of the possibility that more or less similar compounds may be involved in biological oxidative processes.[2,3] Quite apart from their possible biological applications, they include novel examples of coordination complexes of a transition element. Elvidge and Lever[2] found that oxidation of pyridine solutions of phthalocyanatomanganese(II) with molecular oxygen resulted in precipitation of short, opaque, purple crystals with a metallic luster. They formulated this substance as $\mathrm{Mn^{IV}PcPyO}$ (Pc = phthalocyanato). We have carried out an X-ray diffraction study of crystals produced in this way which show them to be a more complicated double complex of manganese(III), *viz.*, $(\mathrm{Mn^{III}PcPy})_2\mathrm{O}$.

A preliminary account of these results has been published elsewhere.[4] In this paper we give more extensive details of the structure which resulted after more exhaustive refinement.

Experimental Section

Preparation.—The crystals were prepared by adding 100 mg of phthalocyanatomanganese(II) to 50 ml of pyridine. After stirring for 2 hr in dry air the solution was filtered through a sintered-glass funnel to remove any undissolved $\mathrm{Mn^{II}Pc}$. The deep blue solution was concentrated at room temperature by evaporation in a stream of dry nitrogen until opaque, purple crystals having a metallic luster were observed. They were removed from the mother liquor by filtration and stored in a sealed vial containing an atmosphere saturated with pyridine until ready for use. Exposure of the crystals to air results in the loss of some of the pyridine of crystallization. For this reason, as well as the fact that analytical results on similar classes of compounds are frequently in error owing to incomplete combustion of the sample, chemical analyses are not sufficient per se to determine accurately the empirical formula. Furthermore, several possible empirical formulas, including Lever's $\mathrm{Mn^{IV}PcPyO}$,[2] are within the range of accuracy of the analytical results.

Anal. Calcd for $(\mathrm{MnPcPy})_2\mathrm{O}\cdot2\mathrm{Py}$ ($\mathrm{C_{84}H_{52}Mn_2N_{20}O}$): C, 68.75; H, 3.57; N, 19.10. Found: C, 67.68; H, 3.57; N, 19.00.

Crystals of the complex obtained by treating $\mathrm{Mn^{IV}Pc(OH)_2}$ with pyridine[5] in air were identical in color, shape, and diffraction pattern with those of $(\mathrm{Mn^{III}PcPy})_2\mathrm{O}\cdot2\mathrm{Py}$ prepared as previously described.

X-Ray Diffraction.—Early work on the complex was hampered by poor diffraction patterns. Subsequently, this was attributed to loss of pyridine of crystallization. The crystal used in the present investigation (0.15 × 0.15 × 0.30 mm) was sealed in a thin-walled glass capillary with a drop of pyridine in the other end.

X-Ray photographs obtained by precession and Weissenberg methods, using Cu Kα radiation, established the orthorhombic symmetry of the crystal. The crystal was then transferred to a General Electric XRD-5 goniostat equipped with a scintillation counter and a pulse height discriminator. The unit cell dimensions were then measured and are based on λ 1.54051 A for Cu Kα_1. The intensities of 3156 independent reflections ($2\theta < 80°$) were measured by the stationary-crystal, stationary-counter technique, counting for 10 sec/reflection. The data were corrected for Lorentz and polarization effects. No corrections were made for extinction or absorption ($\mu R \sim 1$). Careful measurements with the counter detected no violations of the extinction rules for space group $P2_12_12_1$; similar measurements of Laue-equivalent reflections detected differences corresponding to point symmetry 222 and later served to establish the absolute configuration of the specimen.

Calculations were made on IBM 7044 and CDC 6600 computers using full-matrix least-squares and Fourier programs written by Zalkin. The function $\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2$ was minimized.

Atomic scattering factors for neutral C, H, Mn, N, and O given by Ibers[6] were used. The real part of the anomalous dispersion correction[7] ($\Delta f' = -0.5$) was applied to the scattering factor for manganese and the imaginary part (($\Delta f'' = 3.0$) was included in the refinement.

Results

Unit Cell and Space Group.—The unit cell is orthorhombic with dimensions: $a = 22.635 \pm 0.005$, $b = 23.850 \pm 0.005$, $c = 12.808 \pm 0.003$ A, and $V = 6717.1$ A^3. The space group is $P2_12_12_1$ with each cell containing four asymmetric units that consist of $(\mathrm{MnPcPy})_2\mathrm{O}\cdot2\mathrm{Py}$ or $\mathrm{C_{84}H_{52}Mn_2N_{20}O}$ (107 atoms excluding

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[2] J. A. Elvidge and A. B. P. Lever, *Proc. Chem. Soc.*, 195 (1959).

[3] G. Englesma, A. Yamamoto, E. Markham, and M. Calvin, *J. Phys. Chem.*, **66**, 2517 (1962).

[4] L. H. Vogt, A. Zalkin, and D. H. Templeton, *Science*, **151**, 569 (1966).

[5] A. B. P. Lever's method for preparing his $\mathrm{Mn^{IV}PcPyO}$ complex: private communication.

[6] J. A. Ibers in "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202.

[7] D. H. Templeton, ref 6, p 214.

hydrogen). Because of solubility problems, the molecular weight could not be determined by the usual methods; however, from the volume of the asymmetric unit and density measured by flotation (1.41 g/ml at 25°), a molecular weight of 1469 was determined compared to 1467.3 calculated from the empirical formula.

Determination of the Structure.—The structure determination was surprisingly straightforward and lacked any special difficulty except excessive arithmetic. The two Mn positions were located from the Patterson function. A sequence of least-squares and three-dimensional Fourier calculations, coupled with the assumption that the phthalocyanine rings would have essentially the same shape as determined[8] in other crystals, led to the structure. To refine the 107 atoms required 439 parameters including a scale factor, coordinates, anisotropic parameters for each manganese atom, and individual isotropic thermal parameters for the other atoms. The least-squares program on our IBM 7044 (32 K memory) computer can handle 160 parameters in a full-matrix calculation. The refinement procedure was started with this program, refining about one-third of the structure at a time. At 2 hr/run, this procedure required 6 hr to shift each parameter.

The program was modified to neglect all off-diagonal elements of the matrix. This change permitted all parameters to be shifted in 1 hr, and more refinement per hour of computer time was realized. Each of the 3156 measured intensities (3048 were nonzero intensities) was given unit weight and was included in the refinement. This procedure was followed through the final, full-matrix refinement described later. The discrepancy index

$$R = \sum||F_o| - |F_c|\sum|/|F_o|$$

which was 0.48 for the two manganese atoms, was reduced to 0.084 for 107 atoms. The anomalous dispersion effect of manganese was included in the calculations and was sufficient to establish the absolute configuration of the structure[9] (by comparison of unweighted R values). The full-matrix least-squares program was then modified for the larger capacity CDC 6600 (132 K memory) computer which could refine all of the 439 parameters in one pass (about 1.25 hr). A comparison of the final agreement factors and atomic coordinates from each method of refinement showed that both methods gave essentially the same results, *viz.*, R(diagonal matrix) = 0.084 and R(full matrix) = 0.083.

The final atom coordinates and thermal parameters are presented in Tables I and II. Figures 1 and 2 show the atom numbering system and ring orientation, respectively. The largest shift was 0.002 A in the last cycle of refinement. The observed and calculated structure factors are given in Table III. Attempts to

Table I

Final Coordinates and Isotropic Thermal Parameters together with Their Standard Deviations, for All Atoms except Hydrogen

ATOM[a]	x	y	z	B[b]	x 10⁴			
					σ(x)	σ(y)	σ(z)	σ(B)
Mn(A)	0.0231	0.1210	0.0857	c	1	1	2	c
Mn(B)	.0664	.0740	-.1543	c	1	1	2	c
OXYGEN	.0453	.0964	-.0330	3.3	4	4	7	0.2
NPNA	-.0048	.1544	.2335	4.1	5	5	10	.3
C1PNA	.0145	.1303	.3229	5.4	7	7	14	.4
C2PNA	-.0056	.1529	.4221	6.8	9	8	16	.5
C3PNA	-.0390	.2006	.4245	7.4	9	9	17	.5
C4PNA	-.0575	.2232	.3338	8.2	10	9	19	.5
C5PNA	-.0406	.2015	.2332	6.1	8	8	15	.4
N+01A	.1363	.2110	.0806	3.6	5	5	9	.2
C++2A	-.0074	.2314	-.0108	3.1	6	6	11	.3
N++3A	.0342	.1991	.0381	3.2	5	5	9	.2
C++4A	.0860	.2272	.0429	3.8	6	6	11	.3
C++5A	.0771	.2836	-.0076	3.5	6	6	11	.3
C++6A	.1187	.3266	-.0271	5.1	7	7	13	.4
C++7A	.0943	.3763	-.0781	6.7	8	8	16	.4
C++8A	.0369	.3772	-.1054	6.2	8	8	15	.4
C++9A	-.0040	.3340	-.0887	4.8	7	7	13	.4
C++10A	.0213	.2864	-.0375	3.8	6	6	12	.3
NO+1A	-.0607	.2186	-.0348	3.8	5	5	9	.3
C-+2A	-.0837	.1688	-.0146	3.6	6	6	11	.3
N-+3A	-.0586	.1242	.0387	3.8	5	5	9	.2
C-+4A	-.0992	.0818	.0454	3.9	6	6	11	.3
C-+5A	-.1529	.0989	-.0032	4.2	7	6	12	.3
C-+6A	-.2048	.0685	-.0167	5.6	8	7	14	.4
C-+7A	-.2481	.0990	-.0764	6.9	8	8	16	.5
C-+8A	-.2393	.1543	-.1143	7.2	9	9	16	.5
C-+9A	-.1865	.1828	-.0978	5.8	8	7	14	.4
C-+10A	-.1423	.1531	-.0424	4.3	7	6	12	.3
N-01A	-.0900	.0304	.0902	4.7	5	5	10	.3
C--2A	.0508	.0131	.1931	3.3	6	6	11	.3
N--3A	.0091	.0450	.1446	3.5	5	4	9	.2
C--4A	-.0405	.0150	.1344	3.9	6	6	12	.3
C--5A	-.0326	-.0402	.1854	4.8	7	7	13	.4
C--6A	-.0748	-.0867	.1990	6.0	8	7	14	.4
C--7A	-.0483	-.1318	.2576	6.6	8	8	15	.5
C--8A	.0067	-.1319	.2975	6.4	8	8	14	.4
C--9A	.0469	-.0869	.2828	5.0	7	7	13	.4
C--10A	.0239	-.0406	.2231	4.3	7	6	12	.3
NO-1A	.1045	.0262	.2172	3.8	5	5	9	.3
C+-2A	.1309	.0750	.1890	3.0	6	6	10	.3
N+-3A	.1029	.1200	.1414	3.5	5	5	9	.2
C+-4A	.1450	.1603	.1256	4.1	6	6	12	.3
C+-5A	.2007	.1409	.1628	4.6	7	6	13	.4
C+-6A	.2558	.1675	.1608	5.3	7	7	14	.4
C+-7A	.3023	.1355	.2092	6.3	8	8	15	.4
C+-8A	.2911	.0821	.2557	6.1	8	8	15	.4
C+-9A	.2356	.0569	.2525	5.0	7	7	13	.4
C+-10A	.1905	.0872	.2072	4.0	6	6	12	.3
NPNB	.0903	.0450	-.3079	3.3	5	5	9	.2
C1PNB	.0839	-.0088	-.3373	5.2	7	7	14	.4
C2PNB	.0926	-.0283	-.4415	6.2	8	8	15	.4
C3PNB	.1135	.0091	-.5162	5.7	8	8	14	.4
C4PNB	.1202	.0655	-.4848	5.3	7	7	14	.4
C5PNB	.1084	.0820	-.3830	4.0	6	6	11	.3
N+01B	-.0707	.0896	-.2445	4.1	5	5	9	.3
C++2B	-.0084	-.0287	-.1205	3.7	6	6	11	.3
N++3B	-.0017	.0252	-.1626	3.0	4	4	9	.2
C++4B	-.0544	.0396	-.2033	3.4	6	6	11	.3
C++5B	-.0963	-.0080	-.1898	4.2	7	6	12	.3
C++6B	-.1561	-.0123	-.2211	5.2	7	7	13	.4
C++7B	-.1830	-.0649	-.1904	6.7	8	8	15	.5
C++8B	-.1532	-.1044	-.1350	6.9	8	8	15	.5
C++9B	-.0946	-.1001	-.1058	5.6	7	7	14	.4
C++10B	-.0665	-.0484	-.1368	3.7	6	6	11	.3
NO+1B	.0337	-.0566	-.0705	3.7	5	5	9	.3
C-+2B	.0866	-.0374	-.0551	3.7	6	6	11	.3
N-+3B	.1117	.0116	-.0926	3.4	5	5	9	.2
C-+4B	.1662	.0152	-.0533	3.8	6	6	11	.3
C-+5B	.1798	-.0344	.0073	4.0	6	6	11	.3
C-+6B	.2309	-.0483	.0643	5.2	7	7	13	.4
C-+7B	.2282	-.1002	.1210	6.3	8	8	14	.4
C-+8B	.1790	-.1330	.1207	6.4	8	8	15	.5
C-+9B	.1278	-.1199	.0635	5.1	7	7	13	.4
C-+10B	.1295	-.0678	.0067	4.5	7	7	12	.4
N-01B	.2050	.0573	-.0677	4.0	5	5	9	.3
C--2B	.1416	.1771	-.1895	3.3	6	6	11	.3
N--3B	.1369	.1206	-.1541	2.8	4	4	8	.2
C--4B	.1895	.1063	-.1140	3.7	6	6	11	.3
C--5B	.2312	.1537	-.1253	4.0	6	6	12	.3
C--6B	.2901	.1587	-.0938	5.0	7	7	14	.4
C--7B	.3174	.2103	-.1096	6.9	8	8	15	.5
C--8B	.2854	.2560	-.1532	6.6	8	8	16	.4
C--9B	.2253	.2507	-.1885	5.3	7	7	13	.4
C--10B	.1983	.1966	-.1683	4.1	6	6	12	.3
NO-1B	.0987	.2065	-.2287	4.0	5	5	9	.3
C+-2B	.0443	.1890	-.2452	3.2	6	6	11	.3
N+-3B	.0232	.1348	-.2255	3.5	5	5	9	.3
C+-4B	-.0342	.1327	-.2535	3.3	6	6	11	.3
C+-5B	-.0525	.1884	-.2911	4.3	7	7	12	.4
C+-6B	-.1060	.2096	-.3240	4.8	7	7	13	.4
C+-7B	-.1087	.2656	-.3575	5.5	7	7	14	.4
C+-8B	-.0565	.3010	-.3534	5.3	7	7	14	.4
C+-9B	-.0028	.2796	-.3193	4.3	7	6	12	.3
C+-10B	-.0013	.2217	-.2875	4.2	7	6	12	.3
1PM1	.3707	-.2394	-.0052	13.9	17	15	33	1.0
2PM1	.3190	-.2250	.0318	17.3	22	17	34	1.3
3PM1	.2720	-.2415	-.0337	21.1	23	23	48	1.8
4PM1	.2800	-.2603	-.1254	15.8	20	18	35	1.2
5PM1	.3305	-.2777	-.1560	17.3	22	17	35	1.3
6PM1	.3753	-.2449	-.1158	19.6	21	20	41	1.5
1PM2	-.1582	.0781	.5187	14.5	16	17	28	1.1
2PM2	-.1182	.0345	.4947	17.1	19	18	36	1.3
3PM2	-.1229	.0304	.3770	16.2	18	17	35	1.2
4PM2	-.1511	.0719	.3255	16.0	17	19	32	1.2
5PM2	-.1732	.1231	.3624	14.7	16	16	32	1.0
6PM2	-.1851	.1232	.4686	14.4	15	16	32	1.0

[a] See Figure 1 for the atom numbering system. [b] Of the form $\exp(-B\lambda^{-2}\sin^2\theta)$ where B is in A². [c] Treated anisotropically—see Table II.

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(8) J. M. Robertson, *J. Chem. Soc.*, 1195 (1936); J. M. Robertson and I. Woodward, *ibid.*, 219 (1937); 36 (1940).

(9) All molecules in one crystal are of the same handedness, but another crystal from the same preparation is as likely to be right-handed as left-handed. Thus, there is no general significance to the absolute configuration which we found.

TABLE II

FINAL ANISOTROPIC[a,b] THERMAL PARAMETERS OF THE TWO MANGANESE ATOMS

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(A)	4.3	2.5	3.8	0.3	0.2	−0.2
Mn(B)	3.5	2.3	3.8	0.2	0.3	−0.2

[a] Of the form $(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$ with $4\beta_{ij} = a_i{}^*a_j{}^*B_{ij}$, $a_i{}^*$ being the length of the ith reciprocal axis. With this notation B_{ij} are in units of A^2. [b] Estimated standard deviations are all approximately 0.1 A^2.

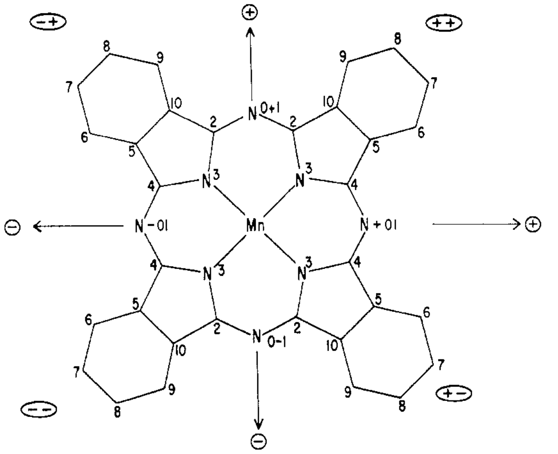

Figure 1.—Atom numbering system. The two phthalocyanine rings are designated "A" and "B" (see Figure 2). For each ring a set of orthogonal axes is drawn through the N+01, Mn, N−01 and N0+1, Mn, N0−1 atoms to separate the molecule into four quadrants. All atoms not otherwise marked are carbons. The atom C++2A is, therefore, the carbon atom marked "2" in the diagram, located in the (++) quadrant of the "A" phthalocyanine ring. The atoms in the coordinated pyridines are designated as NPNA, C1PNB, etc., and refer to the nitrogen atom of the pyridine coordinated to the Mn of the "A" phthalocyanine ring and the first carbon atom in the pyridine coordinated to the Mn of the "B" phthalocyanine ring, respectively. Because of the uncertainties in the exact positions of the atoms in the molecules of pyridine of crystallization (not shown in this figure), differentiation of the carbon and nitrogen atoms was not meaningful. These atoms are designated simply as 1PM1, 6PM2, *i.e.*, first atom of pyridine molecule no. 1 and sixth atom of pyridine molecule no. 2, respectively.

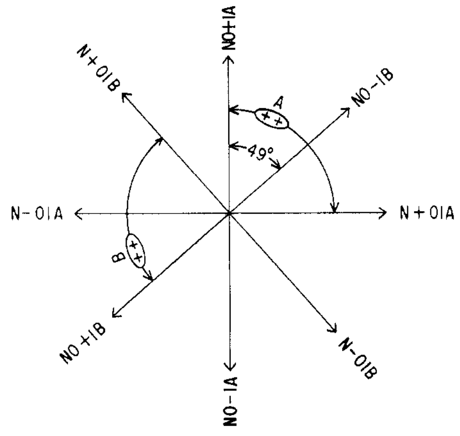

Figure 2.—Diagram representing the relative orientation of the "A" and "B" phthalocyanine rings.

locate the hydrogen atoms on a difference Fourier were unsuccessful.

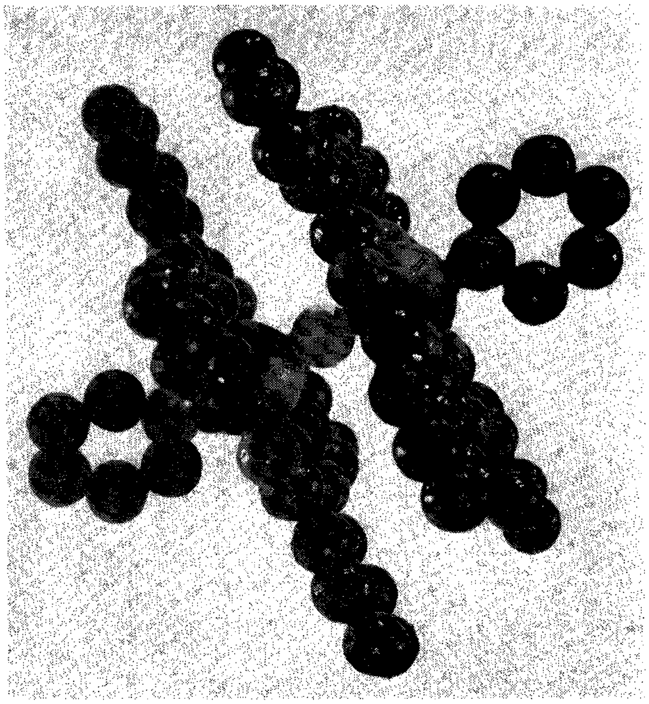

Figure 3.—Photograph of a cork-ball model of the $(MnPcPy)_2O$ molecule. Hydrogen atoms are omitted. For clarity, the Pc rings are half their actual thickness.

Description of the Structure.—The complex (Figure 3) consists of two approximately flat and parallel phthalocyanine ring systems, designated as ring A and ring B, each with a manganese atom at its center. These two ring systems are staggered at 49° with respect to each other so that the phenyl groups on one ring are approximately between the phenyl groups on the other ring. The rings are joined by an oxygen atom which is midway between the two manganese atoms. Each manganese also has a pyridine molecule coordinated opposite to its oxygen atom and oriented so that the plane of the pyridine bisects the (N−01)-Mn-(N+01) angle of the adjacent Pc ring (see Table IV for the atom numbering system). The crystals consist of these complex molecules together with molecules of pyridine of crystallization which are not bonded in any direct way to the complex molecules. The large temperature factors of these pyridines of crystallization suggest disorder or incomplete occupancy of their lattice sites. One of the referees pointed out that these pyridines show bond distances ranging from 1.27 to 1.51 A, bond angles ranging from 104 to 138°, and out-of-plane distances up to 0.25 A. Some important bond distances and angles and their standard deviations are listed in Table IV.

Average values of the lengths and angles of some chemically equivalent bonds are given in Figure 4. These average distances are expected to have standard deviations of the order of 0.01 A. The standard deviations of the bond angles are on the order of 1° or less.

The bond distances and angles are in agreement with results on other phthalocyanines.[8] The Mn-O distance of 1.71 ± 0.01 A is shorter than predicted for a single covalent bond. It is expected that an explanation of the magnetic properties will involve electronic

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS (×2.0) OF PHTHALOCYANATOPYRIDINEMANGANESE(III)-μ-OXO-PHTHALOCYANATOPYRIDINEMANGANESE(III) DIPYRIDINATE

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H,K= 0, 0
L FOB FCA
2 45 33
4 110 103
6 71 69
8 13 11
10 0 22

H,K= 0, 1
L FOB FCA
1 440 544*
2 146 150
3 52 60
4 66 69
5 13 19
6 70 69
7 73 70
8 121 125
9 14 19
10 0 12
11 0 16

H,K= 0, 2
L FOB FCA
0 234 279*
1 44 57
2 125 126
3 306 314
4 33 59
5 45 40
6 15 17
7 41 45
8 35 40
9 119 115
10 0 7
11 19 24

H,K= 0, 3
L FOB FCA
1 173 183
2 73 76
3 335 351
4 194 198
5 70 63
6 25 28
7 24 14
8 21 21
9 71 74
10 31 29
11 0 11

H,K= 0, 4
L FOB FCA
0 173 169
1 39 53
2 38 46
3 149 149
4 152 150
5 33 34
6 252 246
7 138 142
8 67 78
9 61 57
10 0 10
11 39 43

H,K= 0, 5
L FOB FCA
1 433 457
2 78 65
3 76 75
4 178 175
5 32 16
6 63 46
7 53 66
8 116 116
9 98 107
10 42 44
11 23 27

H,K= 0, 6
L FOB FCA
0 292 306
1 21 48
2 104 104
3 41 38
4 42 38
5 42 43
6 167 156
7 40 38
8 14 24
9 113 117
10 0 46
11 0 8

H,K= 0, 7
L FOB FCA
1 41 37
2 205 213
3 115 117
4 60 56
5 58 63
6 144 142
7 70 63
8 51 47
9 0 2
10 43 49
11 11 24

H,K= 0, 8
L FOB FCA
0 95 96
1 147 159
2 71 74
3 12 4
4 151 156
5 49 56
6 113 130
7 34 32
8 0 8
9 73 77
10 55 53

H,K= 0, 9
L FOB FCA
1 45 35
2 143 157
3 138 134
4 165 162
5 108 112
6 34 27
7 95 84
8 29 37
9 41 39
10 55 60

H,K= 0, 10
L FOB FCA
0 52 36
1 228 225
2 27 21
3 292 307
4 20 29
5 83 75
6 38 36
7 26 12
8 0 4
9 0 7
10 11 17

H,K= 0, 11
L FOB FCA
1 115 119
2 134 138
3 143 153
4 90 66
5 96 97
6 17 12
7 126 131
8 19 24
9 37 35
10 20 21

H,K= 0, 12
L FOB FCA
0 233 221
1 28 28
2 57 47
3 86 89
4 20 16
5 9 17
6 159 154
7 0 16
8 64 62
9 16 27

H,K= 0, 13
L FOB FCA
1 55 39
2 178 177
3 37 45
4 82 83
5 61 68
6 10 16
7 0 4
8 0 8
9 16 27

H,K= 0, 14
L FOB FCA
0 127 118
1 38 28
2 67 72
3 217 220
4 53 59
5 20 32
6 61 76
7 27 24
8 0 3

H,K= 0, 15
L FOB FCA
1 80 75
2 21 25
3 0 10
4 124 130
5 94 82
6 0 7
7 25 25
8 0 15

H,K= 0, 16
L FOB FCA
0 10 32
1 60 62
2 26 28
3 70 75
4 67 66
5 74 82
6 27 20
7 60 55

H,K= 0, 17
L FOB FCA
1 48 48
2 56 57
3 187 187
4 76 75
5 19 17
6 16 36
7 25 23

H,K= 0, 18
L FOB FCA
0 33 22
1 24 32
2 153 146
3 19 22
4 41 36
5 54 53
6 16 23

H,K= 0, 19
L FOB FCA
1 153 139
2 0 11
3 43 35
4 111 109
5 83 89

H,K= 0, 20
L FOB FCA
0 151 144
1 104 88
2 28 16
3 59 55
4 38 42

H,K= 0, 21
L FOB FCA
1 11 9
2 41 28

H,K= 1, 0
L FOB FCA
1 195 218*
2 108 106
3 54 54
4 10 8
5 105 97
6 56 61
7 126 126
8 45 49
9 142 147
10 15 30
11 0 16

H,K= 1, 1
L FOB FCA
0 337 396*
1 534 638
2 108 92
3 377 379
4 122 116
5 78 77
6 32 29
7 15 16
8 106 109
9 38 37
10 26 34
11 32 36

H,K= 1, 2
L FOB FCA
0 699 893*
1 61 55
2 277 260
3 587 600
4 345 348
5 69 74
6 40 37
7 17 12
8 29 26
9 53 49
10 56 68
11 71 70

H,K= 1, 3
L FOB FCA
0 27 26
1 93 94
2 285 277
3 503 494
4 297 289
5 129 111
6 39 41
7 48 52
8 130 122
9 32 33
10 0 12
11 0 23

H,K= 1, 4
L FOB FCA
0 47 57
1 198 191
2 356 334
3 90 102
4 242 229
5 65 56
6 230 221
7 66 63
8 13 17
9 105 105
10 27 30
11 0 27

H,K= 1, 5
L FOB FCA
0 50 59
1 199 199
2 207 212
3 125 112
4 105 104
5 105 102
6 45 39
7 66 63
8 45 46
9 39 46
10 15 22
11 30 31

H,K= 1, 6
L FOB FCA
0 103 98
1 56 57
2 188 194
3 107 103
4 135 117
5 90 95
6 61 67
7 72 72
8 59 63
9 93 97
10 16 19
11 23 24

H,K= 1, 7
L FOB FCA
0 31 49
1 110 100
2 28 28
3 63 57
4 117 106
5 84 95
6 73 66
7 95 92
8 71 61
9 89 93
10 54 59
11 11 23

H,K= 1, 8
L FOB FCA
0 157 153
1 235 235
2 141 140
3 156 172
4 63 67
5 38 32
6 17 15
7 36 30
8 0 9
9 32 21
10 42 46

H,K= 1, 9
L FOB FCA
0 60 59
1 123 125
2 89 93
3 94 78
4 33 21
5 137 125
6 67 62
7 89 93
8 25 26
9 27 37
10 0 19

H,K= 1, 10
L FOB FCA
0 110 95
1 113 104
2 81 87
3 108 93
4 35 51
5 57 56
6 132 139
7 28 35
8 53 64
9 51 58
10 61 53

H,K= 1, 11
L FOB FCA
0 82 73
1 80 60
2 203 205
3 21 24
4 31 40
5 84 86
6 75 69
7 52 46
8 15 15
9 0 26
10 30 29

H,K= 1, 12
L FOB FCA
0 36 21
1 76 94
2 49 54
3 203 189
4 30 35
5 39 45
6 69 67
7 31 31
8 19 19
9 11 22

H,K= 1, 13
L FOB FCA
0 22 23
1 83 83
2 72 63
3 20 30
4 90 94
5 107 108
6 25 27
7 72 72
8 25 20
9 39 42

H,K= 1, 14
L FOB FCA
0 22 17
1 67 73
2 65 59
3 40 36
4 40 38
5 61 50
6 79 89
7 48 43
8 34 34

H,K= 1, 15
L FOB FCA
0 86 77
1 48 29
2 110 109
3 48 46
4 101 99
5 47 48
6 32 32
7 54 53
8 48 51

H,K= 1, 16
L FOB FCA
0 137 134
1 61 59
2 70 70
3 119 122
4 44 42
5 84 86
6 16 6
7 60 51

H,K= 1, 17
L FOB FCA
0 20 7
1 61 67
2 60 70
3 36 25
4 71 75
5 67 78
6 79 82
7 30 26

H,K= 1, 18
L FOB FCA
0 142 146
1 21 28
2 40 35
3 29 34
4 83 84
5 45 49
6 28 23

H,K= 1, 19
L FOB FCA
0 24 18
1 52 56
2 25 24
3 42 47
4 28 38
5 11 17

H,K= 1, 20
L FOB FCA
0 35 28
1 51 56
2 16 16
3 63 66
4 47 45

H,K= 1, 21
L FOB FCA
0 42 40
1 45 58
2 23 18

H,K= 2, 0
L FOB FCA
0 648 936*
1 288 339
2 245 247
3 229 244
4 157 164
5 34 46
6 63 62
7 0 10
8 61 59
9 81 88
10 30 38
11 0 18

H,K= 2, 1
L FOB FCA
0 244 273*
1 230 235
2 136 140
3 453 449
4 205 206
5 81 69
6 32 36
7 64 63
8 123 122
9 57 57
10 0 11
11 89 92

H,K= 2, 2
L FOB FCA
0 179 183
1 72 68
2 197 205
3 818 848
4 432 422
5 145 126
6 132 128
7 122 122
8 76 76
9 116 112
10 11 11
11 0 11

H,K= 2, 3
L FOB FCA
0 61 63
1 124 110
2 432 434
3 675 671
4 526 495
5 84 77
6 149 132
7 0 16
8 60 60
9 39 39
10 11 17
11 11 23

H,K= 2, 4
L FOB FCA
0 40 53
1 375 365
2 247 246
3 263 251
4 390 359
5 93 86
6 249 243
7 75 71
8 148 149
9 31 31
10 0 8
11 16 10

H,K= 2, 5
L FOB FCA
0 99 113
1 96 94
2 71 63
3 53 50
4 189 185
5 67 66
6 100 94
7 224 220
8 46 41
9 72 74
10 66 71
11 32 39

H,K= 2, 6
L FOB FCA
0 124 130
1 20 20
2 113 105
3 85 91
4 117 110
5 44 41
6 112 107
7 100 90
8 29 34
9 108 111
10 35 41
11 0 10

H,K= 2, 7
L FOB FCA
0 179 161
1 300 310
2 245 252
3 59 44
4 190 180
5 169 173
6 104 101
7 50 51
8 10 11
9 46 40
10 22 33
11 39 42

H,K= 2, 8
L FOB FCA
0 81 72
1 72 75
2 15 72
3 74 74
4 77 79
5 164 151
6 147 146
7 93 72
8 57 40
9 52 54
10 56 63

H,K= 2, 9
L FOB FCA
0 95 81
1 102 93
2 84 83
3 68 63
4 142 145
5 56 57
6 44 57
7 86 79
8 0 10
9 60 64
10 52 52

H,K= 2, 10
L FOB FCA
0 143 145
1 181 186
2 108 103
3 195 192
4 46 46
5 81 81
6 13 17
7 47 41
8 55 52
9 0 13
10 38 43

H,K= 2, 11
L FOB FCA
0 27 15
1 208 200
2 34 19
3 107 104
4 97 92
5 83 76
6 98 96
7 84 70
8 19 17
9 19 23
10 38 37

H,K= 2, 12
L FOB FCA
0 334 330
1 184 183
2 100 80
3 62 69
4 74 70
5 57 56
6 94 97
7 28 27
8 44 41
9 25 26

H,K= 2, 13
L FOB FCA
0 0 6
1 44 54
2 161 167
3 76 69
4 13 6
5 100 101
6 15 7
7 40 48
8 19 27
9 20 21

H,K= 2, 14
L FOB FCA
0 66 61
1 52 60
2 41 42
3 208 184
4 84 72
5 25 15
6 80 70
7 27 40
8 0 2

H,K= 2, 15
L FOB FCA
0 19 19
1 65 63
2 17 6
3 28 31
4 94 82
5 107 107
6 22 22
7 56 57
8 38 37

H,K= 2, 16
L FOB FCA
0 31 30
1 114 115
2 87 80
3 68 65
4 83 85
5 53 62
6 61 64
7 47 47

H,K= 2, 17
L FOB FCA
0 101 98
1 52 48
2 99 92
3 130 117
4 43 46
5 37 40
6 34 32
7 20 14

H,K= 2, 18
L FOB FCA
0 28 27
1 34 31
2 100 91
3 45 42
4 38 35
5 82 91
6 25 25

H,K= 2, 19
L FOB FCA
0 121 114
1 105 108
2 47 55
3 75 71
4 80 78
5 52 61

H,K= 2, 20
L FOB FCA
0 152 151
1 108 107
2 30 27
3 68 71
4 86 82

H,K= 2, 21
L FOB FCA
0 39 32
1 64 71
2 39 31

H,K= 3, 0
L FOB FCA
1 86 84
2 70 61
4 42 41
3 59 37
5 141 137
6 0 12
7 0 12
8 93 91
9 84 89
10 0 4
11 0 10

H,K= 3, 1
L FOB FCA
0 58 50
1 55 45
2 159 153
3 81 89
4 117 118
5 32 25
6 150 140
7 24 33
8 67 69
9 35 46
10 15 20
11 0 10

H,K= 3, 2
L FOB FCA
0 31 31
1 113 117
2 85 87
3 323 315
4 318 314
5 65 64
6 183 170
7 41 47
8 95 94
9 31 20
10 34 43
11 11 18

H,K= 3, 3
L FOB FCA
0 264 262
1 279 271
2 125 122
3 401 399
4 408 391
5 124 123
6 120 113
7 170 163
8 34 33
9 100 103
10 29 27
11 11 9

H,K= 3, 4
L FOB FCA
0 168 152
1 232 221
2 196 182
3 206 212
4 297 269
5 49 48
6 231 212
7 203 198
8 89 87
9 72 66
10 27 32
11 0 15

H,K= 3, 5
L FOB FCA
0 96 93
1 45 43
2 145 127
3 100 88
4 136 142
5 187 165
6 226 217
7 179 172
8 31 22
9 71 72
10 0 11
11 11 18

H,K= 3, 6
L FOB FCA
0 196 189
1 139 145
2 135 125
3 70 62
4 63 65
5 66 71
6 218 221
7 105 93
8 117 111
9 33 31
10 33 37
11 16 29

H,K= 3, 7
L FOB FCA
0 117 111
1 83 90
2 30 36
3 100 97
4 83 94
5 107 98
6 95 100
7 162 156
8 123 115
9 54 52
10 77 81

H,K= 3, 8
L FOB FCA
0 26 14
1 151 142
2 179 166
3 156 146
4 158 144
5 0 11
6 76 67
7 27 33
8 42 34
9 88 91
10 34 43

H,K= 3, 9
L FOB FCA
0 35 50
1 177 178
2 146 156
3 151 157
4 136 144
5 64 62
6 80 82
7 50 55
8 10 20
9 57 56
10 0 8

H,K= 3, 10
L FOB FCA
0 193 189
1 36 46
2 57 46
3 92 88
4 59 49
5 47 47
6 93 90
7 78 47
8 40 35
9 38 37
10 61 72

H,K= 3, 11
L FOB FCA
0 60 66
1 115 124
2 179 171
3 67 59
4 54 42
5 112 103
6 53 55
7 94 88
8 31 29
9 55 60

H,K= 3, 12
L FOB FCA
0 14 11
1 90 83
2 121 124
3 54 71
4 0 10
5 50 37
6 32 25
7 60 66
8 44 44
9 53 56

H,K= 3, 13
L FOB FCA
0 73 61
1 98 85
2 55 46
3 116 124
4 87 86
5 66 63
6 89 90
7 89 86
8 22 25
9 81 39

H,K= 3, 14
L FOB FCA
0 75 72
1 48 55
2 114 105
3 66 60
4 124 116
5 63 65
6 107 93
7 50 42
8 25 37

H,K= 3, 15
L FOB FCA
0 122 125
1 61 67
2 170 173
3 58 59
4 101 102
5 73 66
6 71 63
7 16 12
8 32 36

H,K= 3, 16
L FOB FCA
0 14 10
1 80 78
2 77 81
3 130 132
4 24 18
5 81 77
6 29 22
7 37 26

H,K= 3, 17
L FOB FCA
0 68 69
1 69 70
2 40 38
3 106 99
4 97 94
5 29 30
6 25 17
7 45 44

H,K= 3, 18
L FOB FCA
0 95 86
1 47 47
2 77 75
3 107 104
4 29 25
5 45 36
6 11 14

H,K= 3, 19
L FOB FCA
0 98 102
1 60 54
2 54 61
3 19 11
4 62 71
5 75 67

H,K= 3, 20
L FOB FCA
0 0 18
1 35 34
2 74 73
3 86 84
4 58 67

H,K= 3, 21
L FOB FCA
0 70 76
1 34 41
2 59 55

H,K= 4, 0
L FOB FCA
0 80 88
1 153 152
2 336 354
3 37 38
4 61 67
5 76 72
6 223 228
7 0 9
8 21 23
9 27 24
10 0 13
11 0 10

H,K= 4, 1
L FOB FCA
0 76 81
1 233 237
2 141 155
3 152 141
4 35 31
5 98 100
6 91 87
7 107 113
8 47 55
9 64 76
10 0 12
11 37 39

H,K= 4, 2
L FOB FCA
0 342 338
1 379 383
2 84 87
3 63 70
4 123 127
5 37 39
6 29 30
7 40 45
8 100 98
9 56 57
10 57 62
11 45 47

H,K= 4, 3
L FOB FCA
0 485 480
1 197 185
2 78 62
3 114 126
4 188 190
5 58 56
6 220 198
7 123 124
8 39 40
9 59 56
10 0 23
11 25 29

H,K= 4, 4
L FOB FCA
0 273 276
1 189 173
2 28 28
3 57 51
4 29 20
5 96 83
6 271 258
7 125 118
8 223 221
9 61 55
10 56 59
11 32 34

H,K= 4, 5
L FOB FCA
0 147 137
1 117 96
2 41 56
3 113 102
4 34 32
5 193 187
6 286 287
7 373 358
8 88 83
9 83 80
10 83 80
11 38 41

H,K= 4, 6
L FOB FCA
0 75 71
1 154 156
2 105 98
3 132 127
4 119 105
5 81 81
6 251 237
7 225 211
8 132 131
9 145 138
10 16 14
11 32 37

H,K= 4, 7
L FOB FCA
0 198 188
1 245 243
2 129 120
3 75 74
4 145 132
5 154 151
6 107 92
7 150 141
8 40 36
9 53 61
10 58 54

H,K= 4, 8
L FOB FCA
0 79 86
1 91 87
2 36 31
3 111 107
4 98 81
5 26 27
6 91 91
7 127 126
8 21 20
9 53 61
10 82 83

H,K= 4, 9
L FOB FCA
0 41 48
1 142 148
2 132 131
3 169 171
4 101 95
5 44 44
6 87 78
7 24 22
8 81 82
9 19 26
10 75 72

H,K= 4, 10
L FOB FCA
0 252 228
1 107 92
2 241 250
3 155 144
4 34 32
5 31 30
6 30 21
7 25 26
8 35 41
9 46 52
10 16 17

H,K= 4, 11
L FOB FCA
0 27 32
1 27 42
2 62 56
3 126 116
4 101 99
5 31 38
6 102 108
7 40 47
8 0 8
9 62 64

H,K= 4, 12
L FOB FCA
0 193 188
1 54 35
2 60 65
3 42 49
4 102 104
5 33 25
6 70 44
7 95 99
8 40 36
9 67 65

H,K= 4, 13
L FOB FCA
0 79 80
1 152 145
2 90 84
3 109 97
4 90 78
5 158 151
6 0 16
7 15 12
8 19 28
9 28 27

H,K= 4, 14
L FOB FCA
0 41 46
1 108 105
2 142 134
3 169 142
4 97 89
5 46 54
6 40 35
7 51 42
8 0 11

H,K= 4, 15
L FOB FCA
0 21 6
1 113 111
2 14 11
3 53 47
4 73 61
5 80 83
6 70 67
7 76 78
8 11 13

H,K= 4, 16
L FOB FCA
0 22 24
1 47 58
2 116 134
3 81 74
4 50 58
5 34 34
6 83 86
7 39 35

H,K= 4, 17
L FOB FCA
0 88 90
1 53 57
2 126 132
3 88 92
4 42 41
5 37 37
6 47 51

H,K= 4, 18
L FOB FCA
0 15 8
1 26 12
2 39 38
3 125 128
4 66 71
5 11 15
6 52 51

H,K= 4, 19
L FOB FCA
0 64 58
1 40 38
2 16 44
3 51 63
4 52 53
5 65 69

H,K= 4, 20
L FOB FCA
0 28 29
1 53 48
2 16 11
3 105 106

H,K= 4, 21
L FOB FCA
0 47 43
1 23 22

H,K= 5, 0
L FOB FCA
1 262 286
2 162 177
3 120 119
4 162 159
5 120 107
6 34 31
7 22 30
8 71 62
9 0 9
10 66 63
11 45 40

H,K= 5, 1
L FOB FCA
0 178 167
1 188 159
2 138 127
3 33 34
4 77 79
5 61 58
6 83 74
7 15 22
8 55 55
9 36 35
10 50 48
11 11 22

H,K= 5, 2
L FOB FCA
0 72 64
1 67 70
2 164 175
3 81 68
4 36 26
5 38 45
6 129 124
7 48 39
8 98 95
9 18 24
10 19 20
11 0 11

H,K= 5, 3
L FOB FCA
0 134 126
1 262 245
2 155 148
3 67 58
4 56 54
5 109 124
6 42 37
7 124 129
8 22 23
9 98 97
10 74 73
11 30 38

H,K= 5, 4
L FOB FCA
0 173 171
1 93 100
2 171 164
3 128 122
4 42 40
5 89 76
6 86 87
7 181 174
8 102 103
9 80 70
10 59 43
11 0 19

H,K= 5, 5
L FOB FCA
0 275 280
1 135 133
2 151 146
3 105 105
4 128 130
5 256 239
6 155 152
7 188 174
8 22 24
9 86 89
10 43 44
11 56 58

H,K= 5, 6
L FOB FCA
0 318 323
1 97 100
2 148 148
3 95 88
4 108 109
5 162 151
6 162 168
7 173 172
8 106 106
9 32 43
10 80 84

H,K= 5, 7
L FOB FCA
0 62 63
1 26 17
2 89 83
3 71 71
4 81 99
5 83 74
6 121 112
7 161 159
8 91 91
9 11 9
10 162 143

H,K= 5, 8
L FOB FCA
0 24 27
1 28 26
2 178 184
3 166 160
4 68 69
5 15 20
6 46 45
7 31 32
8 21 23
9 118 116
10 126 143

H,K= 5, 9
L FOB FCA
0 178 166
1 104 105
2 57 37
3 55 44
4 170 160
5 77 76
6 94 100
7 50 45
8 21 21
9 0 11
10 91 96

H,K= 5, 10
L FOB FCA
0 130 113
1 135 124
2 67 57
3 48 54
4 107 89
5 78 64
6 26 15
7 101 102
8 24 23
9 52 54
10 38 44

H,K= 5, 11
L FOB FCA
0 144 123
1 172 170
2 34 25
3 94 103
4 156 152
5 112 99
6 105 100
7 42 37
8 102 104
9 0 12

H,K= 5, 12
L FOB FCA
0 48 45
1 25 17
2 130 132
3 130 118
4 86 92
5 72 63
6 31 34
7 63 58
8 68 76
9 49 49

H,K= 5, 13
L FOB FCA
0 33 28
1 130 125
2 105 104
3 71 57
4 41 36
5 53 54
6 90 98
7 53 50
8 39 38

H,K= 5, 14
L FOB FCA
0 80 99
1 48 45
2 145 148
3 29 26
4 83 78
5 117 122
6 98 93
7 58 61
8 16 13

H,K= 5, 15
L FOB FCA
0 50 60
1 87 93
2 65 62
3 97 92
4 123 119
5 72 63
6 38 29
7 45 55
8 28 28

H,K= 5, 16
L FOB FCA
0 67 80
1 42 41
2 32 24
3 93 84
4 68 76
5 57 60
6 34 34
7 20 22

H,K= 5, 17
L FOB FCA
0 31 35
1 50 51
2 79 69
3 67 60
4 43 38
5 93 83
6 87 89

H,K= 5, 18
L FOB FCA
0 37 36
1 51 45
2 84 91
3 51 51
4 79 66
5 20 33

H,K= 5, 19
L FOB FCA
0 16 19
1 37 31
2 75 78
3 45 48
4 41 46

H,K= 5, 20
L FOB FCA
0 20 10
1 50 52
2 16 22
3 51 54

H,K= 5, 21
L FOB FCA
0 25 21

H,K= 6, 0
L FOB FCA
0 19 17
1 159 179
2 24 28
3 89 82
4 17 21
5 77 76
6 79 82
7 27 31
8 0 8
9 26 35
10 83 90
11 0 6

H,K= 6, 1
L FOB FCA
0 122 123
1 60 64
2 103 107
3 38 58
4 36 44
5 111 111
6 90 91
7 111 111
8 40 36
9 88 86
10 27 30
11 36 49

H,K= 6, 2
L FOB FCA
0 205 201
1 278 269
2 51 55
3 44 45
4 146 147
5 67 66
6 80 75
7 39 39
8 94 97
9 46 45
10 83 87
11 20 26

H,K= 6, 3
L FOB FCA
0 171 179
1 105 100
2 133 139
3 51 54
4 138 136
5 37 41
6 0 8
7 110 104
8 84 85
9 72 70
10 0 8
11 11 24

H,K= 6, 4
L FOB FCA
0 242 254
1 218 220
2 158 163
3 68 58
4 16 19
5 273 265
6 75 78
7 58 55
8 107 104
9 53 58
10 46 47
11 16 23

H,K= 6, 5
L FOB FCA
0 40 23
1 81 85
2 94 91
3 61 85
4 112 96
5 79 65
6 115 117
7 123 118
8 25 14
9 48 57
10 78 82

H,K= 6, 6
L FOB FCA
0 191 191
1 176 157
2 128 121
3 108 112
4 71 77
5 153 150
6 72 85
7 43 42
8 71 66
9 46 42
10 101 105

H,K= 6, 7
L FOB FCA
0 158 165
1 76 90
2 111 115
3 127 127
4 107 101
5 151 123
6 103 100
7 34 27
8 106 97
9 132 134
10 71 81

H,K= 6, 8
L FOB FCA
0 211 211
1 133 115
2 78 64
3 68 65
4 26 24
5 48 35
6 68 60
7 105 109
8 30 33
9 102 95
10 59 62

H,K= 6, 9
L FOB FCA
0 18 10
1 22 24
2 96 83
3 73 75
4 100 100
5 53 45
6 146 140
7 43 40
8 101 97
9 69 71
10 61 76

H,K= 6, 10
L FOB FCA
0 59 52
1 215 206
2 205 196
3 22 23
4 46 48
5 64 55
6 20 13
7 82 62
8 42 41
9 79 75

H,K= 6, 11
L FOB FCA
0 20 24
1 97 99
2 113 109
3 98 86
4 18 12
5 53 48
6 100 91
7 51 49
8 45 30
9 100 98

H,K= 6, 12
L FOB FCA
0 194 190
1 100 100
2 103 101
3 76 70
4 108 117
5 129 129
6 43 48
7 75 70
8 22 22
9 23 26

H,K= 6, 13
L FOB FCA
0 80 76
1 84 89
2 94 96
3 64 55
4 116 120
5 45 49
6 52 56
7 27 29
8 25 30

H,K= 6, 14
L FOB FCA
0 51 44
1 28 24
2 73 80
3 85 82
4 111 109
5 56 45
6 102 97
7 71 68
8 42 49

H,K= 6, 15
L FOB FCA
0 68 57
1 111 117
2 72 64
3 69 70
4 26 21
5 53 44
6 127 126
7 0 13

H,K= 6, 16
L FOB FCA
0 18 29
1 60 76
2 54 52
3 59 53
4 52 48
5 54 58
6 70 74
7 72 73

H,K= 6, 17
L FOB FCA
0 51 47
1 53 48
2 32 27
3 73 65
4 44 50
5 45 34
6 30 31

H,K= 6, 18
L FOB FCA
0 39 35
1 49 45
2 22 13
3 39 38
4 95 98
5 44 37

H,K= 6, 19
L FOB FCA
0 22 16
1 32 27
2 49 43
3 69 66
4 28 37

H,K= 6, 20
L FOB FCA
0 0 10
1 44 31
2 38 40
3 62 62

H,K= 7, 0
L FOB FCA
1 243 270
2 38 38
3 59 63
4 109 103
5 40 47
6 0 4
7 23 17
8 63 65
9 0 4
10 33 30
11 54 53

H,K= 7, 1
L FOB FCA
0 39 30
1 147 143
2 154 161
3 35 32
4 67 71
5 71 80
6 82 79
7 66 62
8 73 75
9 86 75
10 0 21
11 16 26

H,K= 7, 2
L FOB FCA
0 66 61
1 323 333
2 126 126
3 31 31
4 45 33
5 68 72
6 118 114
7 137 134
8 48 52
9 21 25
10 57 61
11 32 35

H,K= 7, 3
L FOB FCA
0 166 147
1 64 71
2 117 129
3 137 143
4 45 49
5 45 42
6 71 72
7 61 72
8 39 45
9 77 80
10 30 36

H,K= 7, 4
L FOB FCA
0 73 83
1 171 172
2 74 73
3 94 95
4 44 46
5 21 22
6 15 12
7 53 57
8 60 47
9 32 38
10 80 74

H,K= 7, 5
L FOB FCA
0 203 213
1 72 75
2 127 131
3 146 153
4 57 59
5 76 78
6 158 158
7 65 65
8 83 84
9 34 24
10 44 48

H,K= 7, 6
L FOB FCA
0 189 180
1 152 137
2 107 123
3 66 71
4 139 139
5 45 47
6 62 62
7 137 125
8 15 19
9 48 52
10 23 21

H,K= 7, 7
L FOB FCA
0 53 57
1 168 163
2 83 96
3 154 140
4 45 40
5 68 72
6 44 42
7 59 57
8 56 58
9 19 46
10 70 75

H,K= 7, 8
L FOB FCA
0 124 124
1 216 213
2 121 118
3 49 53
4 65 60
5 130 131
6 56 49
7 72 69
8 57 52
9 121 119
10 117 132

H,K= 7, 9
L FOB FCA
0 17 25
1 167 168
2 150 150
3 35 28
4 46 52
5 83 74
6 52 40
7 25 29
8 127 125
9 82 80

H,K= 7, 10
L FOB FCA
0 177 177
1 81 82
2 82 74
3 39 34
4 59 68
5 141 140
6 73 71
7 77 75
8 47 44
9 20 15

H,K= 7, 11
L FOB FCA
0 84 79
1 47 51
2 75 72
3 67 65
4 144 148
5 22 15
6 41 42
7 46 43
8 100 98
9 70 74

H,K= 7, 12
L FOB FCA
0 41 47
1 44 43
2 84 89
3 112 111
4 90 90
5 86 85
6 81 83
7 45 39
8 48 43

H,K= 7, 13
L FOB FCA
0 53 59
1 85 92
2 123 118
3 97 98
4 37 32
5 72 64
6 32 38
7 29 24
8 53 48

H,K= 7, 14
L FOB FCA
0 33 19
1 85 81
2 31 23
3 30 33
4 78 82
5 111 105
6 11 23
7 63 53
8 16 12

H,K= 7, 15
L FOB FCA
0 25 25
1 49 57
2 54 58
3 121 111
4 126 127
5 49 54
6 22 26
7 64 80

H,K= 7, 16
L FOB FCA
0 62 61
1 59 61
2 43 46
3 62 61
4 94 96
5 59 59
6 41 55

H,K= 7, 17
L FOB FCA
0 19 19
1 24 17
2 50 35
3 56 53
4 22 21
5 50 50
6 76 76

H,K= 7, 18
L FOB FCA
0 53 46
1 41 47
2 29 31
3 53 51
4 36 32
5 28 31

H,K= 7, 19
L FOB FCA
0 11 13
1 36 27
2 41 43
3 54 56
4 25 22

H,K= 7, 20
L FOB FCA
0 0 11
1 23 18
2 25 28

H,K= 8, 0
L FOB FCA
0 9 16
1 276 284
2 131 125
3 64 70
4 55 52
5 94 99
6 91 95
7 104 101
8 10 13
9 0 5
10 75 66

H,K= 8, 1
L FOB FCA
0 23 32
1 133 136
2 170 165
3 119 112
4 97 92
5 56 55
6 45 49
7 51 51
8 52 50
9 51 53
10 0 5

H,K= 8, 2
L FOB FCA
0 70 81
1 173 192
2 181 185
3 49 47
4 160 156
5 109 99
6 48 59
7 48 47
8 68 66
9 22 20
10 74 72

H,K= 8, 3
L FOB FCA
0 62 63
1 78 93
2 126 115
3 34 36
4 91 94
5 40 33
6 121 114
7 63 55
8 29 32
9 22 17
10 19 16

H,K= 8, 4
L FOB FCA
0 43 35
1 127 135
2 75 61
3 91 94
4 62 65
5 121 121
6 42 54
7 100 103
8 56 59
9 71 81
10 34 40

H,K= 8, 5
L FOB FCA
0 167 167
1 197 196
2 101 105
3 85 89
4 35 26
5 12 9
6 53 50
7 42 37
8 39 36
9 51 58
10 61 63

H,K= 8, 6
L FOB FCA
0 188 205
1 85 84
2 150 135
3 50 48
4 67 68
5 60 59
6 25 27
7 65 67
8 94 89
9 29 25
10 52 47

H,K= 8, 7
L FOB FCA
0 44 41
1 78 59
2 341 330
3 82 81
4 94 92
5 40 43
6 71 74
7 62 61
8 103 104
9 40 44
10 0 13

H,K= 8, 8
L FOB FCA
0 220 218
1 36 33
2 79 79
3 72 63
4 107 107
5 90 95
6 50 51
7 78 83
8 36 35
9 19 10

H,K= 8, 9
L FOB FCA
0 66 75
1 108 100
2 116 118
3 94 97
4 134 129
5 71 68
6 46 41
7 112 112
8 45 70
9 65 68

H,K= 8, 10
L FOB FCA
0 154 151
1 164 162
2 80 74
3 77 66
4 92 91
5 61 63
6 10 5
7 81 83
8 93 90
9 64 67

H,K= 8, 11
L FOB FCA
0 120 121
1 53 60
2 94 95
3 77 75
4 70 66
5 44 43
6 63 69
7 65 55
8 91 85
9 36 39

H,K= 8, 12
L FOB FCA
0 32 39
1 55 60
2 116 110
3 25 18
4 55 53
5 113 110
6 18 16
7 65 58
8 36 36

H,K= 8, 13
L FOB FCA
0 61 50
1 30 29
2 14 9
3 76 78
4 90 88
5 108 94
6 15 9
7 16 14
8 63 61

H,K= 8, 14
L FOB FCA
0 85 86
1 33 14
2 74 73
3 34 32
4 160 144
5 34 33
6 70 65
7 39 37

H,K= 8, 15
L FOB FCA
0 54 59
1 70 70
2 56 60
3 85 83
4 46 46
5 43 47
6 54 47
7 39 44

H,K= 8, 16
L FOB FCA
0 37 39
1 45 48
2 54 51
3 24 12
4 58 61
5 43 38
6 47 47

H,K= 8, 17
L FOB FCA
0 19 9
1 66 63
2 29 28
3 47 44
4 74 70
5 25 20

H,K= 8, 18
L FOB FCA
0 98 99
1 33 30
2 22 29
3 50 57
4 32 34

H,K= 8, 19
L FOB FCA
0 37 43
1 30 32
2 45 40
3 30 35

H,K= 8, 20
L FOB FCA
0 23 11

H,K= 9, 0
L FOB FCA
1 74 64
2 172 186
3 45 37
4 222 240
5 34 29
6 107 102
7 0 7
8 40 50
9 51 57
10 69 71

H,K= 9, 1
L FOB FCA
0 57 52
1 107 104
2 107 113
3 151 187
4 112 97
5 102 112
6 56 96
7 75 76
8 31 40
9 59 62
10 52 52

H,K= 9, 2
L FOB FCA
0 38 38
1 141 146
2 52 98
3 72 67
4 77 70
5 58 63
6 22 32
7 85 82
8 21 18
9 33 34
10 39 38

H,K= 9, 3
L FOB FCA
0 156 166
1 73 78
2 123 126
3 190 184
4 71 71
5 61 62
6 28 27
7 26 23
8 44 41
9 57 63
10 25 22

H,K= 9, 4
L FOB FCA
0 39 49
1 182 185
2 107 112
3 30 28
4 154 148
5 95 96
6 51 49
7 31 30
8 28 37
9 27 29
10 69 68

H,K= 9, 5
L FOB FCA
0 115 133
1 78 83
2 112 111
3 114 116
4 90 81
5 120 116
6 75 75
7 70 74
8 77 75
9 16 6
10 0 4

H,K= 9, 6
L FOB FCA
0 37 39
1 35 54
2 96 101
3 165 156
4 117 107
5 113 113
6 38 32
7 58 60
8 37 36
9 46 48
10 30 28

H,K= 9, 7
L FOB FCA
0 38 30
1 27 16
2 116 115
3 160 163
4 97 99
5 76 73
6 32 34
7 88 85
8 39 46
9 37 39

H,K= 9, 8
L FOB FCA
0 156 138
1 122 109
2 66 73
3 93 91
4 140 139
5 97 90
6 52 43
7 49 45
8 124 122
9 16 20

H,K= 9, 9
L FOB FCA
0 26 31
1 59 59
2 90 89
3 96 95
4 53 55
5 99 95
6 56 50
7 63 54
8 95 93
9 25 31

H,K= 9, 10
L FOB FCA
0 149 150
1 135 125
2 89 76
3 59 55
4 58 54
5 77 81
6 50 45
7 29 30
8 61 60
9 30 36

H,K= 9, 11
L FOB FCA
0 22 13
1 82 89
2 28 30
3 44 41
4 107 105
5 78 85
6 28 31
7 79 82
8 49 54

H,K= 9, 12
L FOB FCA
0 65 63
1 97 95
2 48 30
3 24 24
4 161 163
5 21 25
6 58 55
7 43 46
8 88 84

H,K= 9, 13
L FOB FCA
0 92 101
1 108 97
2 59 61
3 78 75
4 108 110
5 73 65
6 69 64
7 16 18

H,K= 9, 14
L FOB FCA
0 67 58
1 57 57
2 0 7
3 31 19
4 97 91
5 57 48
6 25 26
7 63 58

H,K= 9, 15
L FOB FCA
0 33 30
1 48 41
2 88 86
3 83 77
4 54 53
5 45 49
6 37 46

H,K= 9, 16
L FOB FCA
0 19 17
1 85 61
2 0 2
3 102 102
4 64 57
5 89 84
6 47 42

H,K= 9, 17
L FOB FCA
0 126 128
1 40 37
2 25 27
3 32 26
4 16 14
5 23 20
```

TABLE IV

IMPORTANT BOND[a] DISTANCES (IN A) AND ANGLES AND THEIR STANDARD DEVIATIONS

Bond Distances[b]

Intraring Distances

Bond	Ring A	Ring B
Mn - N++3	1.96	1.94
Mn - N-+3	1.96	1.97
Mn - N--3	1.97	1.95
Mn - N+-3	1.96	1.97
N+01 - C++4	1.30	1.35
N+01 - C+-4	1.34	1.32
NO+1 - C++2	1.29	1.33
NO+1 - C-+2	1.32	1.31
N-01 - C-+4	1.36	1.35
N-01 - C--4	1.32	1.35
NO-1 - C--2	1.30	1.30
NO-1 - C+-2	1.35	1.33
N++3 - C++4	1.36	1.35
N++3 - C++2	1.37	1.39
N-+3 - C-+4	1.37	1.35
N-+3 - C-+2	1.38	1.38
N--3 - C--4	1.34	1.35
N--3 - C--2	1.37	1.42
N+-3 - C+-4	1.37	1.36
N+-3 - C+-2	1.38	1.39
C++2 - C++10	1.50	1.42
C++4 - C++5	1.50	1.49
C-+2 - C-+10	1.43	1.45
C-+4 - C-+5	1.43	1.44
C--2 - C--10	1.46	1.40
C--4 - C--5	1.47	1.48
C+-2 - C+-10	1.41	1.41
C+-4 - C+-5	1.44	1.47
C++5 - C++10	1.33	1.36
C-+5 - C-+10	1.42	1.40
C--5 - C--10	1.38	1.38
C+-5 - C+-10	1.41	1.41
C++5 - C++6	1.41	1.43
C-+5 - C-+6	1.39	1.42
C--5 - C--6	1.47	1.41
C+-5 - C+-6	1.41	1.39
C++6 - C++7	1.46	1.44
C-+6 - C-+7	1.44	1.43
C--6 - C--7	1.44	1.39
C+-6 - C+-7	1.44	1.39
C++7 - C++8	1.36	1.36
C-+7 - C-+8	1.41	1.37
C--7 - C--8	1.36	1.42
C+-7 - C+-8	1.42	1.46
C++8 - C++9	1.40	1.40
C-+8 - C-+9	1.40	1.41
C--8 - C--9	1.42	1.45
C+-8 - C+-9	1.40	1.40
C++9 - C++10	1.42	1.44
C-+9 - C-+10	1.42	1.43
C--9 - C--10	1.44	1.44
C+-9 - C+-10	1.38	1.43

Other Distances

Bond	Dist.	Bond	Dist
Mn(A) - Mn(B)	3.42	C2PNB - C3PNB	1.39
Mn(A) - 0	1.71	C3PNB - C4PNB	1.40
Mn(B) - 0	1.71	C4PNB - C5PNB	1.39
Mn(A) - NPNA	2.15	C5PNB - NPNB	1.37
Mn(B) - NPNB	2.15	N++3A - N+-3A	2.78
NPNA - C1PNA	1.35	N++3A - N-+3A	2.76
C1PNA - C2PNA	1.45	N--3A - N-+3A	2.78
C2PNA - C3PNA	1.36	N--3A - N+-3A	2.78
C3PNA - C4PNA	1.35	N++3B - N+-3B	2.77
C4PNA - C5PNA	1.44	N++3B - N-+3B	2.76
C5PNA - NPNA	1.38	N--3B - N-+3B	2.75
NPNB - C1PNB	1.33	N--3B - N+-3B	2.78
C1PNB - C2PNB	1.43		

Bond Angles

Intraring Angles

The Angle Between	Angles Ring A	Angles Ring B
N++3 - Mn - N-+3	90	90
N-+3 - Mn - N--3	90	89
N--3 - Mn - N+-3	90	90
N+-3 - Mn - N++3	90	90
Mn - N++3 - C++4	124	126
Mn - N-+3 - C-+4	127	126
Mn - N--3 - C--4	126	126
Mn - N+-3 - C+-4	126	125
N++3 - C++4 - N+01	130	128
N-+3 - C-+4 - N-01	125	127
N--3 - C--4 - N-01	128	128
N+-3 - C+-4 - N+01	125	128
C++4 - N+01 - C+-4	123	122
C-+4 - N-01 - C--4	124	121
C++2 - N++3 - Mn	125	128
C-+2 - N-+3 - Mn	125	123
C--2 - N--3 - Mn	124	127
C+-2 - N+-3 - Mn	127	126
N++3 - C++2 - NO+1	129	124
N-+3 - C-+2 - NO+1	128	129
N--3 - C--2 - NO-1	129	125
N+-3 - C+-2 - NO-1	124	126
C++2 - NO+1 - C-+2	123	125
C+-2 - NO-1 - C--2	124	127
C++2 - N++3 - C++4	111	106
C-+2 - N-+3 - C-+4	108	108
C--2 - N--3 - C--4	110	107
C+-2 - N+-3 - C+-4	106	109
N++3 - C++2 - C++10	107	110
N-+3 - C-+2 - C-+10	108	109
N--3 - C--2 - C--10	108	109
N+-3 - C+-2 - C+-10	111	109
N++3 - C++4 - C++5	107	110
N-+3 - C-+4 - C-+5	111	110
N--3 - C--4 - C--5	109	110
N+-3 - C+-4 - C+-5	111	109
C++4 - C++5 - C++10	107	105
C-+4 - C-+5 - C-+10	105	106
C--4 - C--5 - C--10	106	104
C+-4 - C+-5 - C+-10	106	105
C++2 - C++10 - C++5	108	108
C-+2 - C-+10 - C-+5	108	106
C--2 - C--10 - C--5	107	110
C+-2 - C+-10 - C+-5	106	109
C++5 - C++6 - C++7	114	113
C-+5 - C-+6 - C-+7	114	115
C--5 - C--6 - C--7	110	117
C+-5 - C+-6 - C+-7	115	118
C++6 - C++7 - C++8	120	122
C-+6 - C-+7 - C-+8	123	122
C--6 - C--7 - C--8	126	120
C+-6 - C+-7 - C+-8	121	120
C++7 - C++8 - C++9	126	125
C-+7 - C-+8 - C-+9	121	124
C--7 - C--8 - C--9	123	123
C+-7 - C+-8 - C+-9	122	121
C++8 - C++9 - C++10	112	115
C-+8 - C-+9 - C-+10	117	115
C--8 - C--9 - C--10	114	115
C+-8 - C+-9 - C+-10	118	117
C++9 - C++10 - C++5	124	121
C-+9 - C-+10 - C-+5	121	120
C--9 - C--10 - C--5	122	119
C+-9 - C+-10 - C+-5	121	120
C++10 - C++5 - C++6	124	125
C-+10 - C-+5 - C-+6	124	123
C--10 - C--5 - C--6	125	125
C+-10 - C+-5 - C+-6	124	123

Other Angles

Mn(A) - 0 - Mn(B)	178°
NPNA - Mn(A) - 0	178
NPNB - Mn(B) - 0	178
C1PNA - NPNA - C5PNA	122
NPNA - C1PNA - C2PNA	119
C1PNA - C2PNA - C3PNA	120
C2PNA - C3PNA - C4PNA	119
C3PNA - C4PNA - C5PNA	123
C4PNA - C5PNA - NPNA	116
C1PNB - NPNB - C5PNB	116
NPNB - C1PNB - C2PNB	124
C1PNB - C2PNB - C3PNB	119
C2PNB - C3PNB - C4PNB	116
C3PNB - C4PNB - C5PNB	121
C4PNB - C5PNB - NPNB	123

[a] See Fig. 1 for atom numbering system.

[b] The standard deviations of individual bond distances are estimated to be about 0.04 Å, on the basis of the differences between bonds which are chemically equivalent and a comparison witb the known dimensions of benzene rings. These estimates do not apply to the pyridine of crystallization, which appears to have very large and anisotropic thermal motion (B is about 15 to 20 Å^2) and which may have some kind of disorder. The standard deviation of the individual bond angles are estimated to be about 2°.

coupling between manganese atoms through this bond system.

Parts of the phthalocyanine rings deviate significantly from planarity (Table V). This is especially true of the carbon atoms of the eight phenyl groups. These phenyl groups are themselves planar to within 0.02 A but are twisted out of the planes of the Pc rings. A study of the packing model of the crystal shows that there is considerable crowding around the phenyl groups. While the average of the phenyl group C–C bond dis-

TABLE V

DISTANCES (IN A) OF THE ATOMS IN THE TWO PHTHALOCYANINE[a] AND COORDINATED PYRIDINE RINGS FROM THEIR LEAST-SQUARES PLANES[b]

Equations of the Least-Squares Planes, where X, Y, and Z Are the Atom Coordinates in A

Pc Ring A: $0.296X - 0.374Y - 0.879Z + 1.933 = 0$
Pc Ring B: $0.281X - 0.354Y - 0.892Z - 1.572 = 0$
Py A: $-0.811X - 0.585Y - 0.004Z + 2.080 = 0$
Py B: $0.951X - 0.194Y + 0.243Z - 0.777 = 0$

Atom[c]	Dist to LS plane[d]	Atom	Dist to LS plane[d]
Pc Ring A		Pc Ring B	
Mn(A)	0.04	Mn(B)	−0.01
N+01A	0.06	N+01B	0.02
C++2A	−0.06	C++2B	−0.01
N++3A	−0.04	N++3B	0.06
C++4A	0.00	C++4B	0.06
C++5A	0.00	*C++5B*	0.05
C++6A	0.12	*C++6B*	0.07
C++7A	0.08	*C++7B*	−0.01
C++8A	0.00	*C++8B*	−0.12
C++9A	−0.08	*C++9B*	−0.12
C++10A	−0.06	*C++10B*	−0.02
N0+1A	−0.03	N0+1B	−0.07
C−+2A	0.03	C−+2B	−0.08
N−+3A	−0.01	N−+3B	0.10
C−+4A	0.03	C−+4B	−0.03
C−+5A	0.07	*C−+5B*	−0.22
C−+6A	0.14	*C−+6B*	−0.43
C−+7A	0.25	C−+*7B*	−0.66
C−+8A	0.24	*C−+8B*	−0.69
C−+9A	0.15	*C−+9B*	−0.47
C−+10A	0.09	*C−+10B*	−0.25
N−01A	0.04	N−01B	0.02
C−−2A	−0.02	C−−2B	0.00
N−−3A	−0.04	N−−3B	0.04
C−−4A	0.01	C−−4B	0.04
C−−5A	−0.01	*C−−5B*	0.04
C−−6A	−0.04	*C−−6B*	0.01
C−−7A	−0.11	*C−−7B*	−0.07
C−−8A	−0.19	*C−−8B*	−0.16
C−−9A	−0.16	*C−−9B*	−0.10
C−−10A	−0.06	*C−−10B*	−0.04
N0−1A	−0.05	N0−1B	−0.07
C+−2A	−0.01	C+−2B	−0.08
N+−3A	−0.04	N+−3B	0.02
C+−4A	0.06	C+−4B	−0.01
C+−5A	0.19	*C+−5B*	−0.17
C+−6A	0.34	*C+−6B*	−0.31
C+−7A	0.39	*C+−7B*	−0.42
C+−8A	0.27	*C+−8B*	−0.43
C+−9A	0.16	*C+−9B*	−0.30
C+−10A	0.10	*C+−10B*	−0.16
Py Coordinated to Ring A		Py Coordinated to Ring B	
NPNA	0.00	NPNB	0.00
C1PNA	−0.02	C1PNB	0.02
C2PNA	0.03	C2PNB	−0.03
C3PNA	−0.02	C3PNB	0.02
C4PNA	0.01	C4PNB	0.00
C5PNA	0.00	C5PNB	−0.01

[a] The least-squares planes for the Pc rings were determined using all atoms in the rings except the six carbon atoms in each phenyl group—these atoms are in italics. [b] The least-squares planes are not weighted. [c] See Figure 1 for the atom numbering system. [d] The standard deviations are estimated at 0.04 A.

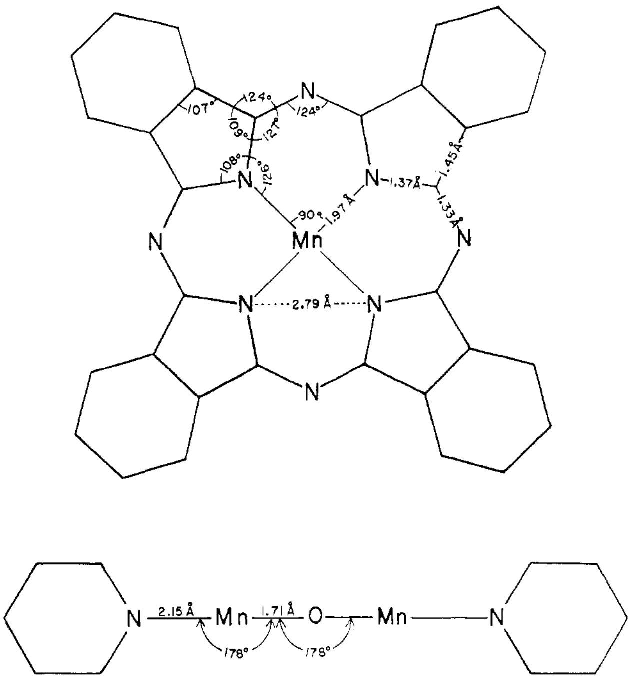

Figure 4.—Average bond distances and angles.

tances is typical (1.41 ± 0.02 A), the bond angles deviate somewhat from the expected 120°. The same two angles in each of the eight phenyl groups (∠5, 6, 7, and ∠8, 9, 10; see Figure 1) are less (average, 115 ± 2°) than the other angles (average, 123 ± 2°). It is not clear whether this situation is (i) an artifact of the methods used to collect the data and refine the structure, (ii) the result of packing forces, or (iii) the result of subtle electronic effects.

The packing model also shows that the staggering of the two Pc rings by 49° rather than 45° is probably due to the coordinated pyridine on the "B" ring being wedged between the phenyl group in the (+ −) quadrant of the "A" ring and the phenyl group in the (− +) quadrant of the "B" ring (see Figure 1). The 97° dihedral angle between the plane of the pyridine coordinated to Mn(B) and the plane of the "B" ring is also considered to arise from molecular packing forces. The corresponding dihedral angle between the "A" ring and its pyridine is 91 ± 2°.

In conclusion, the "irregularities" in the geometry of the $(\mathrm{Mn^{III}PcPy})_2\mathrm{O}$ molecules are considered to arise from molecular packing forces and no chemical significance is assumed except as a reflection of the flexibility of such a large molecule. The mechanisms proposed for the formation of this complex[2,3] need to be reexamined in the light of its formulation as $(\mathrm{Mn^{III}PcPy})_2\mathrm{O}$ rather than $\mathrm{Mn^{IV}PcPyO}$ as previously proposed.

Acknowledgment.—We thank Professor Melvin Calvin for bringing this very interesting substance to our attention.