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The Crystal Structure of the 2 : 3 Complex of Zinc Phthalocyanine and *n*-Hexylamine[1]

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Crystals of the 2 : 3 complex of zinc-phthalocyanine and normal hexylamine were studied. They are monoclinic, space group $P2_1/c$, with cell dimensions $a=12.40$, $b=15.76$, $c=20.05$, $\beta=93.2°$ and there are four phthalocyanine and six hexylamine molecules per cell. The phthalocyanine molecule is not planar and the central zinc ion is displaced from the plane by 0.48 Å toward the nitrogen atom of the amine. Zinc ion is of a square pyramidal five coordination. There are two bonding states for the amine in the complex crystal. One is weakly bonded and can be easily released from the lattice and the other is strongly bonded and coordinated directly to the zinc ion. None of the atomic parameters of these amines except those of the coordinating nitrogen were exactly determined.

Phthalocyanine and its metal derivatives have been regarded as important and being studied in many fields such as pigment industry, solid state physics of organic crystals, catalysis, colloid and coordination chemistry and X-ray crystallography. They assume a common molecular structure similar to porphin derivatives and are of interest also from a biological view point particularly when they form additive complexes with both aliphatic and aromatic amines with respect to Mn[2], Cr[3], Fe[4], and Zn[5] derivatives.

In the course of electron microscopy and X-ray diffraction study on the polymorphic transformation of powdery zinc phthalocyanine which usually takes place in various organic dispersion media, Kobayashi, Uyeda, and Suito[5] found that various additive complexes are produced as crystalline powders stoichiometrically taking up the molecules of amine in which the original powder was dispersed. By means of differential thermal analysis, the molecular ratio of amine molecules to the zinc phthalocyanine matrix was found to depend upon the species of amine itself, whereas the vibrational spectra of these compounds in both rock salt and far infrared regions strongly indicated[6] that the solvated amine molecules are, as strong n-donors, rigidly bound to the central zinc ion with the lone pair electrons of nitrogen atoms. In order to clarify the electronic configuration of the intermolecular bonding which has much to do with the physical properties of the complexes as the biological model or organic semiconductor, the three dimensional structure should be studied in more detail with respect

1) The main part of this work was carried out in the Institute for Protein Research, Osaka University.

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

3) J. A. Elvidge and A. B. P. Lever, *J. Chem. Soc.*, **1961**, 1257.

4) M. Whalley, *ibid.*, **1961**, 866.

5) T. Kobayashi, N. Uyeda, and E. Suito, *J. Phys. Chem.*, **72**, 2446 (1968).

6) T. Kobayashi, N. Uyeda, and E. Suito, *Bull. Inst. Chem. Res. Kyoto Univ.*, **47**, 401 (1969).

to the coordination number of the metal ion, the intermolecular bonding length, the mutual position of the phthalocyanine and solvated molecules. The crystal structure of pyridine complex of phthalocyanatomanganese was determined by Vogt *et al*[7]. to show that the pyridine molecules are perpendicularly conjugated with the nitrogen atoms to the central metal ions, a pair of which are further connected by an oxygen molecule to form a parallel double complex.

Although this result indirectly supported the idea about the molecular structure of the complexes of zinc-phthalocyanine as deduced from the vibrational spectra, no data about their crystal structures have been reported for those with aliphatic amines.

In view of this, three dimensional X-ray analysis has been undertaken with a well defined single crystal of *n*-hexylamine complex as the first example in a series of similar addition compounds of zinc phthalocyanine.

Experimental

Pure zinc phthalocyanine was prepared following the same procedure as described previously.[5] About 0.1 g of the powder zinc phthalocyanine was completely dissolved into 10 m*l* of specially prepared *n*-hexylamine. When the solvent was slowly evaporated at room temperature, purple hexahedral crystals were obtained in various sizes. After identifying the product as the expected complex with a rotation photograph, a crystal of about $0.2 \times 0.2 \times 0.5$ mm was chosen as a specimen for Weisenberg photographs with Ni-filtered Cu$K\alpha$ radiation. Intensity data were recarded on the Weisenberg photographs taken around the *a*-axis up to the ninth layer and around the *b*-axis up to the twelfth layer.

The number of independent reflections thus observed were about 3000 excluding the zero intensity reflections. Intensity data were derived from films prepared by the multiple-film equi-inclination technique. They were then converted to structure amplitudes after the usual Lorentz and polarization factors had been corrected. No correction for absorption was made.

The molecular ratio of *n*-hexylamine to zinc phthalocyanine was determined by thermal gravimetry,[5] and the density of the crystal was measured by the flotation method with an aqueous solution of potassium bromide.

Results

a) Crystal Data. The crystal of the *n*-hexylamine complex of zinc phthalocyanine belongs to the monoclinic system. The unit cell dimensions are

$$a = 12.40\,\text{Å} \pm 0.02$$
$$b = 15.76\,\text{Å} \pm 0.02$$
$$c = 20.05\,\text{Å} \pm 0.05$$
$$\beta = 93.2^\circ \pm 0.5$$
$$V = 3902.6\,\text{Å}^3$$

The systematic absences are recognized for reflections h0l and 0*k*0 with *l* and *k* odd, respectively, indicating that the space group is $p2_1/c$.

b) Number of n-*hexylamine Molecules in a Unit Cell.* The number of *n*-hexylamines relative to that of zinc phthalocyanine was determined by thermal gravimetry. When the complex is heated, decomposition takes place in two stages releasing *n*-hexylamine molecules stepwise at 140 and 180°C. At temperatures higher than 180°C, decomposition is completed leaving pure zinc phthalocyanine of the β polymorph. Thus, the total reaction can be described by the following equation, where *p* and *q* are the numbers of the component molecules in the complex and ZnPc and Am stand for zinc phthalocyanine and amine.

$$(\text{ZnPc})_p(\text{Amine})_q \rightarrow p\text{ZnPc} + q\text{Am}$$

The percentage weight loss W is related to *p* and *q* as follows.

$$W = \frac{q[\text{Am}] \times 100}{p[\text{ZnPc}] + q[\text{Am}]} = \frac{\text{Weight loss} \times 100}{\text{total weight of complex}}$$

where the brackets denote the molecular weights of components. The actual weight loss was determined to be 20.0%, which shows good agreement with the calculated value of 20.8% when $p : q$ is taken to be 2 : 3 (with $p : q = 1 : 1$, $W = 14.9\%$ and with $p : q = 1 : 2$, $W = 25.8\%$). Thus, the calculated density becomes 1.239 g/cm^3 if four phthalocyanine molecules are assumed to exist in the unit cell. Since the actual density was found to be 1.30 g/cm^3 by the floatation method, it seems reasonable to conclude that the unit cell has four zinc phthalocyanine and six *n*-hexylamine molecules.

c) Structure Determination. The coordinates of the zinc ion were derived from a three dimensional Patterson function as $x/a = 0.020$, $y/b = 0.028$, and $z/c = 0.182$. An electron density function was calculated with the phases due to the zinc ion. The Fourier maps showed all the non-hydrogen atoms of zinc phthalocyanine, and the nitrogen atom of a *n*-hexylamine 2.20 Å apart from the zinc ion lying almost in the center of the planar phthalocyanine molecule. The structure factors were calculated using these atomic positions shown in the maps and the atomic parameters were refined three times by successive cycles using the block-diagonal least-squares method. The discrepancy index R was 0.17 at this stage. Although the appearance of a nitrogen atom near the zinc ion indicated that only one *n*-hexylamine is coordinated to a phthalocyanine molecule, the positions of the carbon atoms of *n*-hexylamine could not be distinctly determined, since the electron density maps showed lower peaks at the positions of these atoms with only about one fifth of the peak heights of the carbon atoms in the phthalocyanine ring. With existence probabilities set as one half, the positions of the five carbon atoms of the *n*-hexylamine were added to those of the other well defined atoms. By use of this new set of positions, several cycles of structure factor calculations and least-squares refinements were performed to reach a discrepancy index of 0.15 in the final stage. No information concerning the other two amine molecules was obtained. The final atomic parameters and their thermal parameters are listed in Table 1, and the calculated and observed structure factors are compared in

7) L. H. Vogt, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **6**, 1725 (1967).

TABLE 1. THE POSITIONAL PARAMETERS AND ISOTROPIC THERMAL PARAMETERS

Atom	x	y	z	B	Atom	x	y	z	B
Zn	0.01962	0.02872	0.18170	*	C 12	0.50877	0.12408	0.08408	3.606
N 1	0.10521	−0.04846	0.24766	3.783	C 13	0.45632	0.15766	0.02716	3.664
N 2	0.16137	0.06436	0.14271	2.301	C 14	0.34198	0.15782	0.01901	3.187
N 3	−0.05425	0.05480	0.08941	2.184	C 15	0.28520	0.11969	0.07288	2.302
N 4	−0.10635	−0.05608	0.19602	2.395	C 16	0.16988	0.10414	0.08170	2.556
N 5	0.28715	0.00373	0.22868	2.952	C 17	−0.00722	0.10325	0.03831	2.717
N 6	0.09545	0.12683	0.03538	2.332	C 18	−0.09063	0.11998	−0.01443	1.823
N 7	−0.23224	−0.00763	0.10297	2.447	C 19	−0.09030	0.16462	−0.07564	2.884
N 8	−0.03627	−0.13280	0.29427	3.444	C 20	−0.18392	0.17164	−0.11725	3.682
N 9	−0.01453	0.14412	0.23692	5.166	C 21	−0.28283	0.13293	−0.09682	3.398
C 1	0.06365	−0.10772	0.29404	2.882	C 22	−0.28412	0.08595	−0.03626	2.540
C 2	0.15172	−0.13649	0.34291	3.272	C 23	−0.18578	0.07948	0.00645	2.588
C 3	0.15201	−0.19087	0.40053	4.965	C 24	−0.15921	0.03972	0.07096	2.372
C 4	0.25244	−0.20080	0.43515	5.279	C 25	−0.20204	−0.05155	0.16127	1.713
C 5	0.34347	−0.16660	0.41305	4.617	C 26	−0.28160	−0.10223	0.19443	3.426
C 6	0.34954	−0.10991	0.35705	4.501	C 27	−0.39357	−0.11560	0.18109	4.415
C 7	0.24789	−0.09446	0.32225	3.540	C 28	−0.44634	−0.16863	0.22930	7.114
C 8	0.21643	−0.04190	0.26417	3.349	C 29	−0.38543	−0.20911	0.28275	7.093
C 9	0.26108	0.04780	0.17321	2.404	C 30	−0.27565	−0.19173	0.30019	5.036
C 10	0.34414	0.08805	0.13040	2.284	C 31	−0.22428	−0.13906	0.25132	3.244
C 11	0.45630	0.08377	0.13603	3.397	C 32	−0.11389	−0.10909	0.25095	2.567

The estimated standard deviations for all atoms range from 0.003Å to 0.0365Å and average 0.023Å.

* The anisotropic temperature factor for zinc ion is defined by the expression

$$\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})$$

where $\beta_{11}=0.004467$ $\beta_{22}=0.002933$ $\beta_{33}=0.001438$ $\beta_{12}=-0.000322$ $\beta_{13}=0.000632$ $\beta_{23}=0.000740$

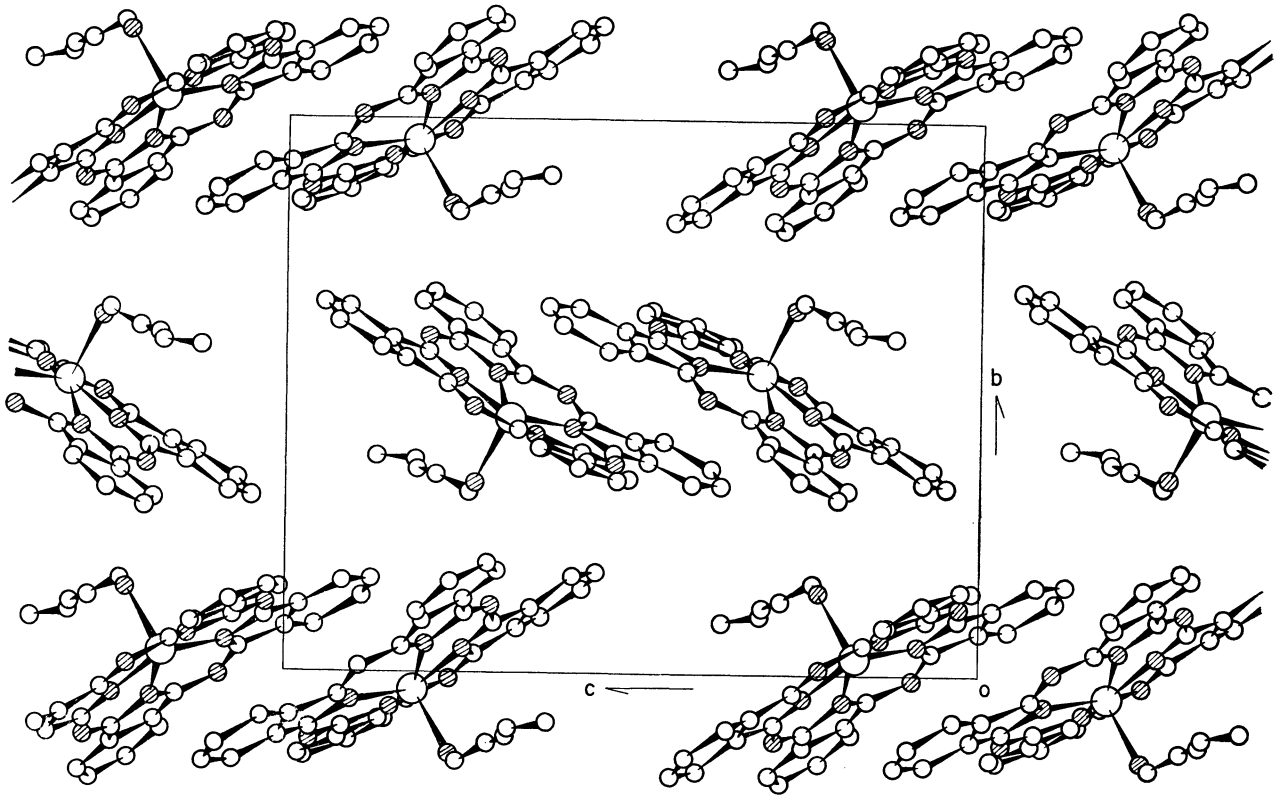

Fig. 1. The crystal structure viewed along the a axis.
◯ : Zn^{2+}, ◍ : N, ○ : C

TABLE 2. OBSERVED AND CALCULATED STRUCTURE FACTORS

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H,L= 0 22			3	59	-51	H,L= 1 22			0	116	-108	5	16	8	H,L= 1-11			3	56	71	7	66	68	0	54	57	8	57	59
0	19	21	4	93	84	0	18	29	1	57	18	6	63	89	11	58	-12	4	46	48	10	27	23	1	26	9	9	59	11
2	25	32	5	23	-14	2	31	28	2	105	108	7	15	-14	12	17	-14	6	18	18	11	23	-13	2	98	-75	10	40	42
4	22	24	6	51	52	4	18	23	3	34	26	8	61	72	13	60	-8	H,L= 2 15			H,L= 2 4			4	76	-75	11	29	5
6	16	-1	7	22	16	H,L= 1 21			4	78	-77	9	25	-17	15	47	-31	2	49	54	0	36	41	5	30	-18	H,L= 2-14		
H,L= 0 21			8	56	49	1	26	45	6	25	-25	10	26	33	19	40	-12	3	34	30	1	52	47	6	35	17	0	50	-51
2	36	43	10	68	66	2	23	29	7	15	5	H,L= 1 -2			H,L= 1-12			4	32	29	3	22	45	7	35	-32	2	49	-43
3	17	16	11	38	34	4	20	18	8	37	30	0	73	-80	0	48	46	5	50	38	4	23	-26	9	48	-52	4	38	-46
4	20	30	13	28	43	H,L= 1 20			10	30	24	1	51	90	1	27	22	8	24	22	5	58	53	11	54	-58	6	33	-32
6	18	10	14	34	-10	3	19	22	H,L= 1 7			2	49	-88	2	19	17	9	25	-18	6	18	22	H,L= 2 -5			H,L= 2-15		
H,L= 0 20			H,L= 0 8			4	19	-20	1	28	-18	3	56	93	3	33	34	10	40	37	7	65	72	1	57	60	1	38	-30
2	20	-16	0	81	-81	5	20	14	2	56	-39	4	47	-62	4	21	24	H,L= 2 14			8	19	17	3	56	51	2	16	-16
3	25	30	2	62	-61	6	20	-22	3	23	-24	5	95	95	5	58	54	0	26	-31	9	69	71	4	67	-63	4	19	-22
4	21	-15	3	37	-26	H,L= 1 19			4	82	-85	6	64	-57	6	27	21	1	19	19	11	46	47	5	39	44	6	19	-32
5	20	20	4	46	-47	1	28	-42	5	27	-25	7	53	61	7	40	36	2	35	-37	H,L= 2 3			6	95	-93	8	34	-31
7	22	18	5	16	9	2	19	19	6	78	-73	8	20	-7	8	28	-24	3	52	32	1	39	-25	7	20	17	H,L= 2-16		
H,L= 0 19			6	15	-11	5	19	-24	8	51	-46	9	30	36	10	35	-33	4	24	-26	2	41	-24	8	53	-51	0	26	22
1	52	-58	9	28	-22	7	41	-23	9	24	19	10	36	39	11	34	31	9	22	19	3	55	-14	9	19	11	2	37	38
4	20	-11	12	34	49	H,L= 1 18			10	46	-50	11	44	50	H,L= 1-13			11	34	24	4	35	34	10	32	-23	4	35	35
6	19	-8	14	28	43	0	26	-28	H,L= 1 6			H,L= 1 -3			1	20	-28	H,L= 2 13			5	32	-28	11	17	-10	7	32	-29
7	20	-15	H,L= 0 7			1	24	23	1	86	-74	2	142	132	3	48	-47	1	47	-49	6	71	73	H,L= 2 -6			H,L= 2-17		
H,L= 0 18			1	16	-15	2	24	-20	2	67	65	4	276	269	4	46	51	2	25	-25	7	25	-28	0	64	56	1	36	31
0	43	-50	3	43	-41	5	45	-46	3	70	-83	5	161	-185	6	28	26	3	31	-59	8	62	65	1	26	24	3	34	39
2	24	-9	6	76	-75	7	50	-52	4	40	48	7	14	3	8	21	25	4	23	-21	10	24	21	2	70	58	9	25	7
3	18	-28	7	59	-53	9	41	-32	5	63	-58	8	62	-55	9	19	-19	8	30	-28	H,L= 2 2			3	68	62	H,L= 2-18		
4	39	37	8	102	-114	H,L= 1 17			6	20	-16	9	58	60	10	36	27	10	31	-30	0	25	-12	4	50	49	0	25	-10
5	45	-50	10	54	-57	1	26	28	7	87	-88	10	15	0	H,L= 1-14			H,L= 2 12			1	23	-19	5	82	-73	7	28	28
6	25	17	11	20	16	2	24	21	9	50	-44	11	29	33	0	60	-69	0	28	-16	2	15	7	6	66	75	H,L= 2-19		
7	36	-36	12	34	-33	6	38	-41	10	19	-11	H,L= 1 -4			2	51	-50	1	29	-27	3	11	-40	7	115	-96	1	47	-48
9	32	-26	H,L= 0 6			7	28	24	11	23	-19	0	121	92	4	43	-43	3	77	-28	5	31	-21	8	88	80	2	31	-36
H,L= 0 17			1	64	-61	8	24	-22	H,L= 1 5			1	121	-126	6	20	-18	4	35	31	6	40	-47	9	16	19	3	30	-31
1	31	28	2	103	94	H,L= 1 16			1	38	48	2	71	39	H,L= 1-15			5	29	-27	7	15	-17	10	28	21	H,L= 2-20		
3	18	24	3	15	12	0	31	29	2	55	-45	4	215	-231	2	22	-30	6	16	13	8	26	-21	11	37	30	0	25	-36
4	20	-21	4	32	29	1	18	15	3	68	71	5	116	143	3	21	-31	7	29	-33	9	54	-55	12	31	-30	2	20	-16
5	37	37	5	34	23	2	41	38	4	18	-15	6	112	-114	4	17	-21	8	41	-32	11	34	-41	H,L= 2 -7			3	23	-28
6	36	-26	6	64	-53	4	46	45	5	9	10	7	49	-60	6	29	12	9	27	-33	H,L= 2 1			1	25	18	4	19	-10
7	28	24	7	65	-58	6	20	26	6	61	45	9	80	79	7	20	16	11	51	-46	1	25	2	2	60	37	H,L= 2-21		
8	24	-17	8	20	-8	7	32	29	7	23	-18	9	83	-106	10	40	-37	H,L= 2 11			3	48	-6	3	19	-3	2	19	-26
H,L= 0 16			9	68	-71	H,L= 1 15			10	18	21	10	16	17	H,L= 1-16			1	51	57	4	58	-57	4	77	67	4	18	-23
0	29	32	11	42	-45	1	19	-23	11	25	-23	11	45	-48	0	45	50	3	21	74	5	8	-2	5	70	-69	H,L= 2-22		
2	47	39	H,L= 0 5			2	19	22	H,L= 1 4			H,L= 1 -5			1	32	-32	5	49	46	6	68	-81	6	47	44	0	23	25
4	35	27	1	51	52	3	31	26	0	86	43	1	37	60	2	32	24	6	18	-21	7	12	17	7	70	75	2	18	25
5	19	19	3	70	72	5	43	32	2	41	24	2	19	-23	3	28	-32	9	34	-27	8	39	-49	8	30	-25	4	16	18
7	22	24	4	68	59	6	25	30	3	85	113	4	69	-77	4	25	21	H,L= 2 10			10	58	-68	9	95	98	H,L= 3 22		
9	32	26	5	62	58	7	36	-30	4	24	30	5	58	62	5	19	13	0	61	53	11	6	-10	10	33	31	0	24	28
H,L= 0 15			6	120	110	8	72	65	5	68	87	6	35	-31	6	26	26	2	34	39	13	31	-6	12	53	70	2	16	18
1	29	-22	8	27	18	9	44	-35	6	19	-6	8	88	-90	9	32	-22	3	75	24	H,L= 2 0			H,L= 2 -8			H,L= 3 21		
5	10	-19	9	36	-31	10	40	45	7	57	52	9	24	22	H,L= 1-17			4	31	26	0	61	-49	0	61	-39	2	18	-8
6	30	32	H,L= 0 4			H,L= 1 14			9	56	64	10	51	-50	1	40	37	5	49	50	1	68	99	1	24	21	5	17	16
7	39	-33	0	39	33	0	56	-57	10	17	15	11	10	-16	3	25	24	6	14	7	2	29	24	2	61	-58	H,L= 3 20		
8	42	40	1	44	-24	2	51	-50	11	32	37	H,L= 1 -6			5	19	25	7	36	30	3	52	-15	3	15	15	0	26	-27
10	40	37	2	36	-37	4	31	-29	H,L= 1 3			0	69	57	6	18	15	9	20	25	4	9	12	4	41	-35	5	19	19
H,L= 0 14			4	42	-45	8	34	-30	1	144	-127	10	8	13	7	22	20	11	43	34	5	28	-37	5	50	50	H,L= 3 19		
0	64	-63	5	61	62	9	52	42	2	171	155	2	61	48	H,L= 1-18			H,L= 2 9			6	33	32	6	58	-65	1	32	-33
1	17	-15	6	29	25	11	24	26	3	133	124	4	69	72	5	19	25	1	62	-58	7	20	30	7	61	65	2	20	-15
2	56	-59	7	66	73	H,L= 1 13			4	93	76	5	54	-47	6	21	19	2	14	13	8	27	27	10	38	33	3	27	-35
4	37	-35	8	33	33	1	41	-32	5	46	-50	6	70	75	7	28	25	3	37	-63	9	14	-18	H,L= 2 -9			H,L= 3 18		
6	36	-32	9	51	58	2	18	-24	9	44	40	7	123	-112	9	26	19	4	40	41	10	20	-40	1	77	-71	0	39	-29
H,L= 0 13			10	16	-9	3	29	-26	11	22	16	8	70	61	H,L= 1-19			5	44	-42	11	15	-14	2	43	43	7	29	-23
1	26	-26	11	33	37	4	30	-26	H,L= 1 2			10	19	10	1	28	-29	6	62	67	12	25	-33	4	11	-9	H,L= 3 17		
3	28	-25	H,L= 0 3			5	33	-32	0	95	-114	11	61	63	3	25	-26	7	34	-28	13	26	5	5	26	-20	1	33	31
5	15	-16	1	82	-67	6	20	-25	1	30	51	14	25	-5	H,L= 1-21			8	49	48	H,L= 2 -1			6	87	-80	2	24	10
6	36	-38	2	130	-135	8	30	-24	2	70	-63	H,L= 1 -7			2	20	-28	11	27	20	1	68	28	7	49	-42	3	28	27
8	39	-41	3	218	-235	10	25	-16	3	83	-53	1	24	-9	4	23	-24	H,L= 2 8			2	207	166	8	33	-17	5	19	12
10	25	-24	4	146	-138	11	24	23	4	22	30	2	52	33	H,L= 1-20			0	99	-90	3	85	-58	9	59	-69	8	23	-24
H,L= 0 12			5	91	-113	H,L= 1 12			5	33	-33	4	65	72	2	20	-27	1	24	17	4	41	35	10	32	-25	H,L= 3 16		
0	70	70	6	37	31	0	43	43	6	37	-31	5	58	-44	4	19	-27	2	122	-112	5	69	65	11	60	-57	0	27	29
1	20	10	7	28	26	1	13	7	7	21	-22	6	39	35	7	21	-23	3	14	29	6	48	50	H,L= 2-10			2	43	41
2	51	49	8	51	50	2	53	59	8	13	-9	7	48	44	H,L= 1-22			4	91	-91	7	12	0	0	12	1	4	39	36
3	23	14	9	53	50	3	30	-33	9	72	-83	9	49	52	4	21	30	6	40	-34	8	74	75	1	51	47	H,L= 3 15		
4	21	18	10	21	-11	4	52	47	10	46	51	10	68	67	H,L= 2 22			8	17	-25	9	7	-5	2	39	39	1	35	-26
5	32	-26	11	26	23	5	46	-47	11	42	-46	13	47	0	0	25	29	9	19	10	10	29	24	4	19	14	2	51	49
6	27	24	H,L= 0 2			9	38	-32	H,L= 1 1			H,L= 1 -8			4	17	15	11	26	-17	11	15	-16	5	80	-78	3	32	21
7	61	-67	0	154	-191	11	45	-48	1	36	39	0	69	-66	H,L= 2 21			H,L= 2 7			12	30	32	6	14	-15	5	27	24
9	34	-31	1	92	-147	H,L= 1 11			2	50	-87	2	56	-60	1	19	25	1	39	-49	13	32	-36	7	78	-87	8	24	25
10	35	-31	2	71	-120	1	105	98	3	40	24	4	30	-42	3	19	10	3	74	10	14	32	35	9	76	-71	10	39	34
12	28	-26	3	83	-136	2	16	10	4	20	-4	5	38	38	4	19	23	4	39	-46	H,L= 2 -2			10	44	-46	H,L= 3 14		
H,L= 0 11			4	53	-65	3	87	93	5	10	8	6	32	-25	H,L= 2 20			5	12	-4	0	32	-62	11	23	-20	0	36	-49
1	83	84	5	72	-67	5	53	53	6	57	-65	7	23	17	4	21	-14	6	66	-72	1	12	8	12	42	-55	1	36	31
3	78	75	6	34	-24	6	15	-9	7	8	-6	8	37	-23	5	19	17	8	58	-57	2	59	-45	H,L= 2-11			2	53	-55
4	14	9	7	31	-37	H,L= 1 10			8	59	-65	9	25	22	6	19	-14	10	26	-26	3	83	105	1	46	51	3	48	43
5	34	29	9	25	-31	0	29	-25	10	50	-63	11	33	31	H,L= 2 19			11	21	14	4	53	-57	3	47	53	4	35	-27
8	19	-13	10	28	19	1	12	17	11	19	-23	H,L= 1 -9			1	46	-49	H,L= 2 6			5	46	50	5	48	42	11	37	31
11	50	-47	11	46	-51	2	33	37	12	33	-44	2	58	39	3	23	-15	0	82	74	6	5	5	H,L= 2-12			H,L= 3 13		
14	33	-8	12	38	38	3	43	48	H,L= 1 0			3	10	-13	H,L= 2 18			2	66	55	7	57	54	1	33	31	1	55	-60
H,L= 0 10			H,L= 0 1			4	44	39	0	245	240	4	43	-45	0	36	-35	3	37	-70	8	27	24	2	31	25	3	37	-38
0	58	46	2	36	117	5	53	48	2	153	175	5	40	-38	1	25	24	4	101	98	9	61	77	3	54	57	4	19	-17
1	15	-2	3	50	23	7	36	39	3	28	-20	6	85	-77	5	19	-21	5	85	-84	10	16	12	4	47	46	5	28	-25
3	30	23	4	106	-115	9	43	34	4	34	37	7	45	-38	7	45	-42	6	72	68	11	25	22	5	49	44	6	21	-23
4	19	21	5	72	-81	11	23	20	5	19	-30	8	56	-52	9	25	-21	7	59	-59	H,L= 2 -3			6	27	26	H,L= 3 12		
5	66	61	6	52	-63	H,L= 1 9			6	35	23	10	22	-16	H,L= 2 17			8	22	14	1	85	-96	7	60	58	0	50	-37
6	38	27	7	24	26	1	126	-115	8	13	8	H,L= 1-10			1	34	31	9	43	-42	2	90	79	8	29	20	1	25	20
7	62	58	8	75	-59	2	75	69	9	20	-18	0	88	86	2	24	22	11	20	-18	3	127	-113	11	24	24	2	20	-18
9	48	43	10	38	-36	3	82	-69	10	37	-47	1	14	2	3	23	8	H,L= 2 5			5	64	-52	H,L= 2-13			4	43	33
10	25	10	H,L= 0 0			4	60	61	11	13	-12	2	40	35	6	28	-28	1	98	103	6	44	44	1	20	-19	5	51	-53
11	48	49	2	240	250	5	20	-17	H,L= 1 -1			3	20	-20	8	30	-29	2	15	-17	7	43	32	2	61	65	6	14	12
13	28	20	4	278	-288	6	64	62	1	135	165	5	86	-85	H,L= 2 16			3	46	36	9	22	17	3	30	-31	7	43	-42
H,L= 0 9			6	46	23	8	45	39	2	49	-103	7	64	-64	0	31	26	4	20	3	9	31	24	4	46	41	8	42	-43
1	42	-43	8	40	26	10	35	33	3	87	98	9	45	-40	1	23	14	5	68	63	11	8	13	5	22	-24	9	27	-27
2	28	-27	14	35	-39	H,L= 1 8			1	20	-2	11	51	-48	2	46	47	6	76	-22	H,L= 2 -4			6	33	28	10	31	-29

TABLE 2. Continued

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
11	34	-34	7	47	-58	1	19	-13	H,L=	4	20	H,L=	4	6	1	20	18	0	46	44	2	22	20	H,L=	5	1	0	19	12
H,L=	3	11	8	37	-37	2	54	-54	0	24	-25	0	42	-42	2	17	-15	1	27	26	3	39	-38	1	10	-15	2	33	-28
1	27	26	9	26	-25	3	13	19	3	18	19	1	81	-77	3	55	48	2	47	43	5	45	-49	3	19	-15	3	28	34
2	40	39	10	31	-27	4	34	-61	5	26	29	2	34	25	5	72	62	3	44	45	6	17	-12	4	67	-69	4	51	-47
3	53	55	H,L=	3	1	5	43	44	H,L=	4	19	3	86	-80	6	18	-16	4	28	27	7	28	-26	5	19	17	5	50	47
4	15	7	1	24	8	6	25	-14	1	32	-36	4	67	64	7	60	63	5	35	31	9	36	-27	6	71	-76	6	21	-18
5	49	48	2	50	-47	7	25	18	3	33	-27	5	34	-29	9	62	56	7	30	33	11	29	-27	7	15	-12	7	38	31
6	48	-45	3	10	2	9	41	42	H,L=	4	18	6	23	-12	10	19	16	9	39	29	H,L=	5	11	8	37	-47	9	29	33
8	29	-21	4	43	-55	11	44	49	1	30	-27	7	54	-61	11	44	47	H,L=	4	-13	1	51	58	9	22	-20	11	33	34
9	44	-45	6	68	-67	H,L=	3	-9	3	31	-33	8	39	-33	H,L=	4	-3	2	51	53	2	18	-17	10	44	-40	H,L=	5	-9
11	34	-36	9	80	-93	2	38	21	5	19	-14	9	49	-46	1	92	-86	3	26	-29	3	50	61	11	21	20	1	74	-63
H,L=	3	10	9	15	13	3	48	-40	7	28	-21	11	22	-20	2	18	-11	4	51	45	4	56	-67	12	30	-41	2	13	5
0	51	44	10	35	-35	4	30	-38	H,L=	4	17	H,L=	4	5	3	88	-79	5	16	-12	5	58	57	H,L=	5	0	3	70	-68
2	38	34	H,L=	3	0	5	59	-59	2	27	-29	1	10	3	4	80	-40	6	43	51	6	21	-16	0	32	21	4	9	6
3	18	12	0	65	57	6	75	-74	3	35	35	2	20	-14	5	105	-92	7	24	19	10	27	-23	1	40	-31	5	38	-26
4	47	43	1	49	-30	7	26	-21	4	34	-35	3	120	120	6	39	-33	8	51	48	H,L=	5	10	2	50	50	6	22	-18
5	56	58	2	65	46	8	22	-12	5	18	20	4	64	-52	7	27	-30	10	31	30	0	58	50	3	9	-1	8	24	-27
6	36	35	3	10	-8	9	24	-20	6	19	-24	5	54	51	9	15	5	H,L=	4	-14	2	49	48	4	92	80	11	34	36
7	39	39	4	41	33	10	23	21	8	25	-26	7	26	-20	11	14	20	0	44	-42	3	14	7	5	14	10	H,L=	5	-10
10	24	-17	6	41	39	11	39	-35	H,L=	4	16	8	38	35	H,L=	4	-4	2	48	-51	4	39	49	6	36	28	0	47	-35
11	29	25	8	50	53	H,L=	3	-10	0	45	46	10	28	22	0	29	-28	4	35	-41	6	42	35	7	73	-70	2	14	-9
H,L=	3	9	10	14	17	0	74	58	2	36	35	1	10	3	1	31	-19	H,L=	4	-15	9	32	32	8	16	-13	5	37	-36
1	79	-63	11	10	-9	1	34	25	3	34	-9	2	20	-14	2	79	-61	1	60	-57	H,L=	5	9	9	61	-59	6	22	-23
2	46	-38	H,L=	3	-1	2	28	23	4	30	30	3	120	120	3	116	-112	2	36	-31	2	33	31	10	16	-17	7	66	-71
3	23	10	2	21	11	3	27	-20	6	20	11	4	64	-52	4	87	-82	3	34	-37	3	24	-21	11	26	-25	9	22	-24
4	52	63	3	28	48	4	26	-24	H,L=	4	15	5	54	51	5	108	-110	4	59	-60	4	27	23	H,L=	5	-1	10	35	32
5	37	28	4	57	51	5	82	-78	1	28	-19	7	26	-20	6	34	-32	5	25	-25	5	15	-17	1	23	28	11	29	-21
6	78	73	5	41	33	7	82	-83	3	26	22	8	38	35	7	74	-72	6	49	-49	6	67	65	2	66	69	H,L=	5	-11
8	45	41	6	98	106	9	60	-58	4	19	19	10	28	22	9	56	-51	8	26	-30	8	55	64	3	150	146	1	77	48
10	33	34	7	29	27	10	51	-47	6	45	36	H,L=	4	4	10	20	17	H,L=	4	-16	10	30	30	4	56	41	3	32	52
11	32	31	8	77	90	H,L=	3	-11	8	24	34	0	38	26	11	20	-20	1	18	-18	H,L=	5	8	5	63	62	4	23	-23
H,L=	3	8	9	9	14	1	62	63	10	22	22	1	34	27	H,L=	4	-5	2	28	-24	0	62	-63	7	37	-29	5	17	14
0	158	-170	10	47	46	3	41	33	H,L=	4	14	3	36	36	1	54	44	3	46	-50	2	76	-84	8	16	16	6	23	-22
1	20	19	H,L=	3	-2	5	38	35	0	74	-84	4	26	25	2	37	-26	5	51	-54	3	21	21	H,L=	5	-2	8	26	-23
2	66	-72	0	93	-56	6	13	-8	1	25	15	5	26	36	3	33	28	6	28	27	4	45	-45	0	40	-29	10	25	-17
4	13	0	1	37	18	7	22	13	2	55	-57	6	43	38	4	76	-74	7	36	-35	5	27	23	1	52	37	H,L=	5	-12
6	30	-21	2	25	-27	8	24	-23	4	20	-22	7	76	77	5	41	32	H,L=	4	-17	7	41	39	2	18	12	0	48	53
7	16	13	3	26	33	9	18	16	6	20	-15	8	23	-19	6	67	-71	1	36	32	8	31	-31	3	47	48	2	41	41
9	24	17	4	13	-7	10	30	-34	7	40	34	9	57	61	8	49	-46	3	25	28	9	52	43	4	37	29	4	36	38
H,L=	3	7	5	53	61	H,L=	3	-12	H,L=	4	13	11	33	39	9	22	-12	5	28	29	H,L=	5	7	5	44	42	5	16	16
1	60	-49	6	20	-15	1	34	30	1	50	-52	H,L=	4	3	10	47	-42	H,L=	4	-18	1	53	-52	7	57	58	H,L=	5	-13
2	37	-37	7	75	76	2	34	32	3	47	-48	1	80	-79	11	22	1	0	47	45	2	12	-8	8	16	-17	2	43	36
3	29	-21	8	23	-18	3	66	56	4	17	-8	3	30	-26	H,L=	4	-6	2	41	40	3	27	-30	9	49	52	4	30	29
4	48	-49	9	48	56	4	48	43	5	26	-28	4	63	65	0	113	114	3	19	18	4	25	-27	11	30	29	5	36	-41
6	44	-44	11	40	43	5	52	55	6	21	-16	5	43	-39	1	24	20	5	18	19	5	30	-26	H,L=	5	-3	7	28	-23
7	19	-11	H,L=	3	-3	6	57	62	9	32	11	6	63	64	2	92	86	7	23	23	6	43	-46	1	125	-123	8	34	31
8	41	-46	1	28	-39	7	72	74	H,L=	4	12	7	55	-63	3	40	40	9	39	35	8	33	-27	2	33	-25	10	31	34
10	47	-45	2	72	-66	8	41	34	2	15	11	8	25	23	4	79	71	H,L=	4	-19	H,L=	5	6	3	60	-60	H,L=	5	-14
11	16	12	3	80	-81	9	49	52	3	45	-37	9	17	-14	5	35	26	5	17	-13	0	53	43	4	26	17	0	48	-42
H,L=	3	6	4	55	-62	H,L=	3	-13	4	29	20	10	41	42	6	22	19	H,L=	4	-20	1	51	-34	5	47	-38	2	40	-42
0	74	74	5	22	-19	1	35	-39	5	69	-64	11	41	39	8	42	-45	0	20	-16	3	71	-75	6	34	34	3	19	-7
1	66	-55	6	19	5	2	80	80	7	19	-23	H,L=	4	2	10	22	-15	2	19	-25	5	77	-77	7	32	-23	4	34	-38
2	104	88	8	34	-26	3	23	-21	9	20	-22	0	132	-112	11	21	25	4	20	-26	7	41	-41	H,L=	5	-4	6	35	-32
3	83	-67	11	41	36	4	50	51	11	29	-30	1	18	-5	H,L=	4	-7	H,L=	4	-22	9	56	-33	0	109	-85	7	28	21
4	62	56	H,L=	3	-4	5	41	44	H,L=	4	11	2	71	-68	1	32	34	0	22	30	10	23	11	1	15	-6	H,L=	5	-15
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6	12	8	1	76	-64	7	47	43	2	14	10	4	37	-51	4	105	87	H,L=	5	22	H,L=	5	5	3	39	-39	3	20	-19
7	55	-55	2	90	-66	8	57	57	3	38	47	5	21	-23	6	61	61	0	15	23	1	14	25	4	85	-76	4	28	-28
9	46	-55	3	65	-65	10	40	41	4	28	-31	6	96	-108	7	40	-29	H,L=	5	20	2	74	-66	5	48	-46	6	28	-29
10	26	28	5	83	-79	H,L=	3	-14	5	70	64	7	21	-21	8	55	61	3	17	19	3	41	38	6	35	-34	8	24	-15
11	21	-16	6	64	52	0	53	-57	6	58	-57	8	35	-48	9	27	-23	5	24	35	4	55	-46	7	50	-41	H,L=	5	-16
H,L=	3	5	7	88	-84	2	58	-66	7	23	15	9	24	-19	10	65	64	H,L=	5	19	5	21	25	8	17	-12	3	16	-20
1	113	120	9	52	-60	4	27	-33	9	42	-36	10	31	30	H,L=	4	-8	1	27	-28	6	19	-13	9	51	-47	5	28	-34
2	36	-20	11	42	-45	5	19	-15	11	29	-32	12	25	33	0	82	-76	3	22	-21	7	23	21	H,L=	5	-5	6	20	23
3	109	92	H,L=	3	-5	H,L=	3	-15	H,L=	4	10	H,L=	4	1	2	45	-38	H,L=	5	18	8	26	19	1	36	33	7	21	-25
4	11	-3	1	63	52	1	62	-45	0	54	59	2	47	-33	3	20	14	2	28	-28	9	19	-11	2	29	-24	9	26	-28
5	54	59	2	29	-24	2	37	-36	2	44	50	3	25	-6	4	41	-38	3	22	-23	10	29	26	4	50	-40	H,L=	5	-17
6	9	4	3	42	30	3	33	-31	3	19	19	4	47	-46	5	47	45	4	34	-36	11	18	-17	6	57	-54	1	44	48
7	42	30	4	45	-25	4	68	-68	4	19	23	5	20	-17	6	24	-22	5	23	-29	H,L=	5	4	8	48	-45	3	21	18
9	24	19	5	20	19	5	19	-23	5	24	18	6	51	-60	7	46	37	7	22	-26	1	16	16	10	42	-40	5	19	18
10	20	19	6	85	-83	6	67	-60	6	22	22	7	13	-14	9	37	40	8	22	-6	3	16	18	H,L=	5	-6	H,L=	5	-18
H,L=	3	4	7	60	64	8	24	-26	8	20	15	8	56	-71	11	43	46	H,L=	5	17	4	31	25	0	114	112	0	46	42
0	48	20	8	60	-68	H,L=	3	-16	9	31	31	10	55	-63	H,L=	4	-9	2	52	-47	5	32	33	1	23	13	2	36	37
1	9	23	9	17	-12	0	19	23	10	21	-14	12	31	-36	1	42	-44	4	38	-40	7	48	53	2	124	114	5	18	13
2	22	27	10	37	-28	3	34	-30	11	29	36	H,L=	4	0	2	15	-8	6	46	-46	9	56	64	4	62	63	7	20	29
3	46	51	11	24	-19	5	48	-57	H,L=	4	9	0	112	102	3	66	-57	H,L=	5	16	10	17	-19	6	31	29	H,L=	5	-19
5	60	57	H,L=	3	-6	6	20	17	1	26	-26	1	29	11	4	22	-21	0	35	31	11	44	48	7	23	17	1	16	17
6	8	-15	0	101	98	7	29	-33	2	18	21	2	99	101	5	28	-23	2	31	30	H,L=	5	3	9	20	-16	H,L=	5	-20
7	51	52	2	30	24	H,L=	3	-17	3	22	-19	3	18	13	6	35	-38	3	18	-15	1	13	-17	10	32	-23	2	19	-16
9	41	42	3	32	-28	1	52	59	4	29	34	4	78	69	8	26	-25	4	20	18	2	26	24	11	18	-14	H,L=	6	21
11	49	55	4	11	19	3	25	20	5	42	31	5	29	-21	9	21	23	8	25	6	3	31	16	H,L=	5	-7	5	15	9
H,L=	3	3	6	54	48	5	23	14	6	64	58	6	47	48	10	24	20	H,L=	5	15	4	66	61	1	137	125	H,L=	6	20
1	70	-74	7	14	8	H,L=	3	-18	8	77	72	7	40	-34	11	33	27	1	36	30	5	36	-26	2	31	30	3	16	18
2	97	66	8	36	32	3	25	20	10	41	44	8	36	34	H,L=	4	-10	3	18	14	6	44	44	3	37	31	H,L=	6	19
3	76	-76	9	14	14	5	18	18	11	19	13	9	37	-34	0	21	11	4	42	31	7	48	-45	4	58	56	1	22	-28
4	42	54	11	29	25	7	24	27	H,L=	4	8	10	16	6	1	51	-52	6	46	35	8	34	38	5	25	21	3	17	-17
5	72	-76	12	42	-47	9	25	28	0	121	-115	11	36	-35	2	26	24	10	24	23	10	38	38	6	65	65	5	19	-12
6	25	21	H,L=	3	-7	H,L=	3	-19	1	21	15	H,L=	4	-1	3	65	-59	H,L=	5	14	11	38	35	8	26	26	H,L=	6	18
7	44	-71	2	45	-32	1	37	-40	2	71	-67	1	121	115	5	57	-60	0	39	-28	12	29	38	9	20	-18	0	20	-23
8	48	47	3	68	-62	3	24	-26	3	48	40	2	88	72	6	15	-9	5	48	40	H,L=	5	2	10	29	34	2	23	-23
9	19	-18	4	54	60	4	21	5	6	46	32	3	80	74	7	60	-52	6	46	-29	0	117	-110	1	137	125	3	18	-22
10	42	41	5	25	18	5	19	-20	9	46	40	4	68	54	8	23	23	7	50	44	1	41	28	2	31	30	8	20	2
H,L=	3	2	6	53	49	H,L=	3	-20	10	25	-5	5	56	45	H,L=	4	-11	H,L=	5	13	2	23	-1	3	37	31	H,L=	6	17
0	148	-97	7	58	51	0	21	-27	H,L=	4	7	6	50	48	1	49	51	1	44	-42	3	17	-8	4	58	56	2	31	-41
1	32	-24	8	51	56	2	24	-29	1	65	-58	7	59	59	2	42	-39	3	36	-32	4	29	20	5	25	21	4	30	-32
2	63	-60	9	14	13	H,L=	3	-22	3	30	-30	8	48	46	3	58	62	5	19	-24	5	43	-44	6	65	65	6	34	-25
3	11	-9	10	58	52	0	26	40	4	26	-26	9	31	30	4	29	-26	6	18	-12	6	72	-80	8	26	26	H,L=	6	16
4	70	-77	11	21	-16	2	27	38	6	46	-43	10	39	35	5	21	18	7	20	-22	8	43	-42	9	20	-18	0	21	14
5	21	-10	H,L=	3	-8	H,L=	4	22	8	56	-60	H,L=	4	-2	8	28	-26	H,L=	5	12	10	53	50	10	29	34	2	19	21
6	65	-47	0	57	-58	0	23	26	10	38	-32	0	21	-16	H,L=	4	-12	0	16	-6	12	34	54	H,L=	5	-8	3	18	-17

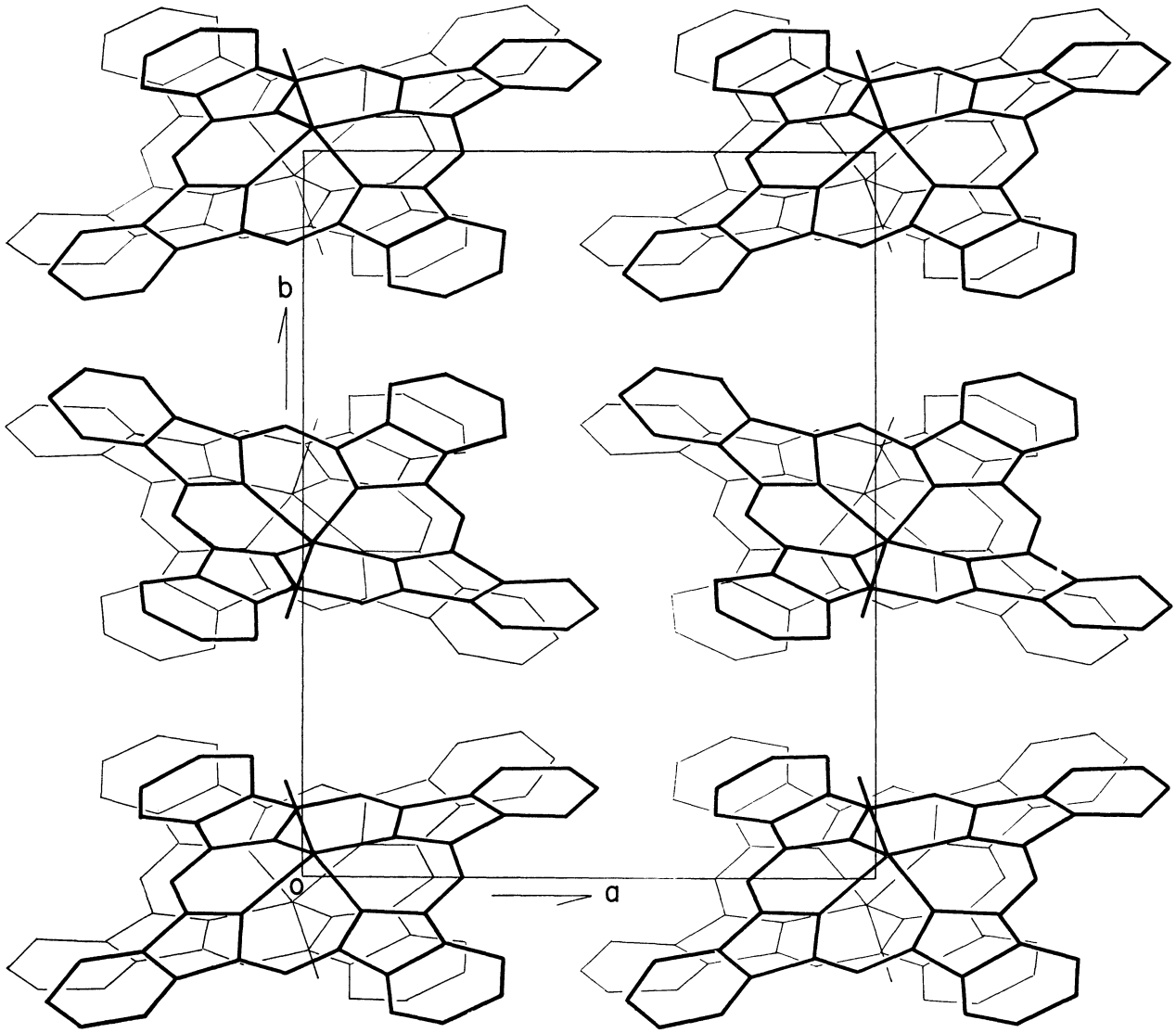


Fig. 2. The crystal structure viewed along the *c* axis.

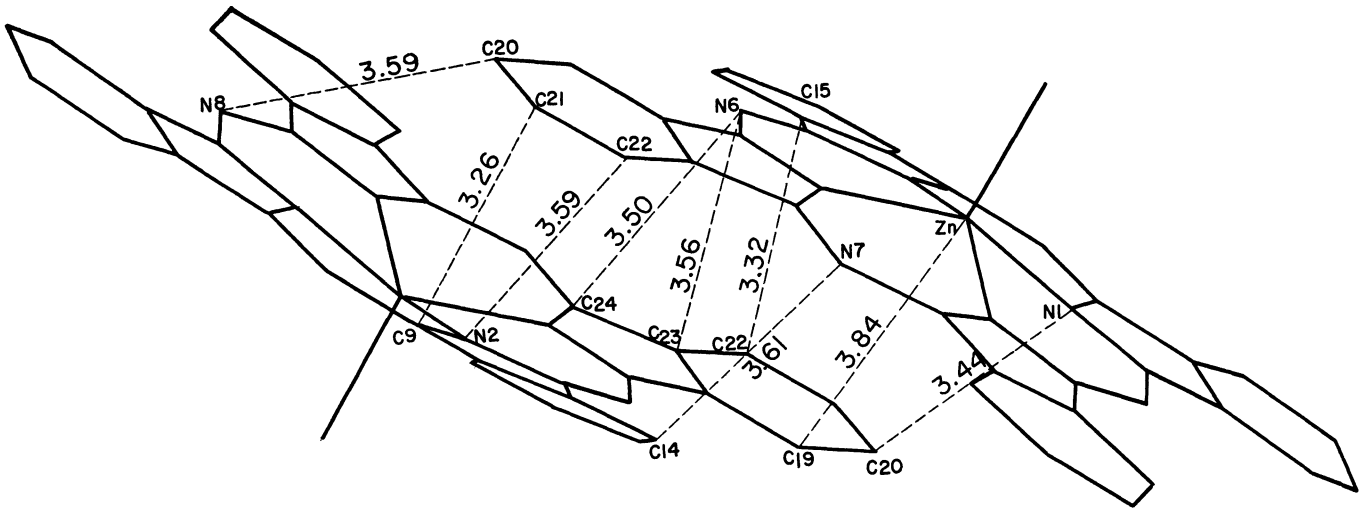


Fig. 3. Intermolecular distances between the paired molecules. The mean estimated standard deviation is about 0.023Å.

Table 2.[8] The atomic scattering factors for C, N, and Zn^{2+} were taken from International Tables for X-ray Crystallography, Vol. III (1962). Refinement was carried out on a HITAC 5020E of the University of Tokyo with the programs written by one of us (T.

8) The complete data of the F_o-F_c table are kept as Document No. 7110 in the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and remitting ¥300 in advances for photoprints. (by check or money order payable to: Chemical Society of Japan).

A.). Figure 1 and 2 show the (100) and (001) projections of the structure. The zinc phthalocyanine molecules make a pair in the crystal and intermolecular distances between these paired molecules are also illustrated in Fig. 3.

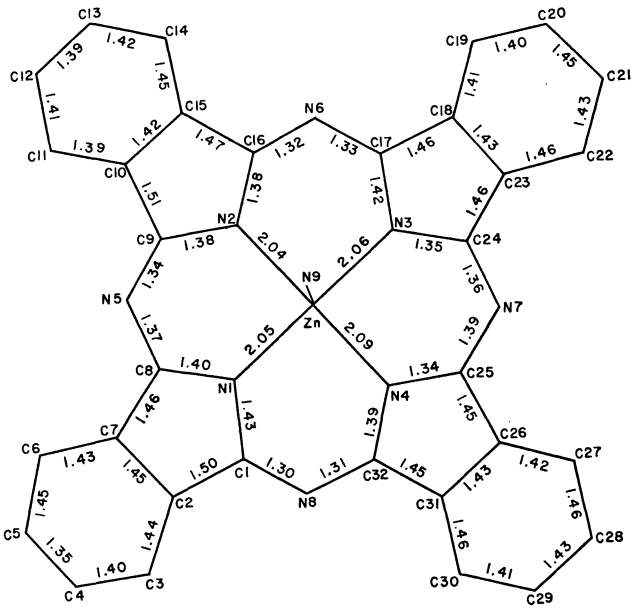
Discussion

Bond distances and bond angles are given in Fig. 4-(a) and (b) only for a phthalocyanine molecule and the nitrogen atom of *n*-hexylamine bonded to it. The central zinc ion is coordinated to five nitrogen atoms, assuming a square pyramidal configuration as a whole. The four nitrogen atoms of pyrrole rings, N1 through N4, define a perfect plane with a shift of ±0.008 Å. The least-squares equation for this plane is

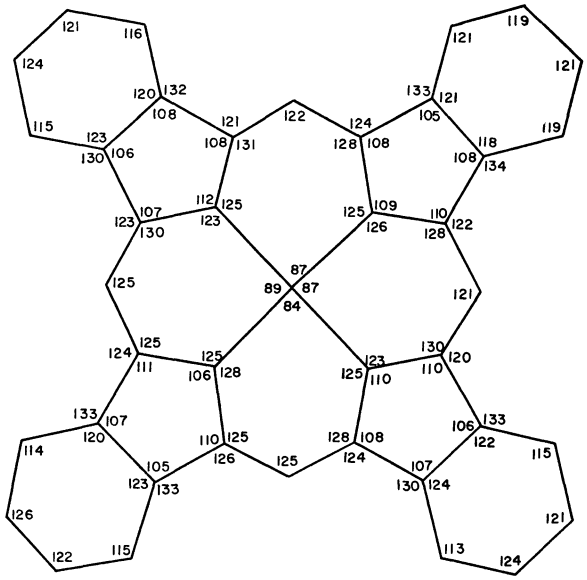
$$0.2671X - 0.7864Y - 0.5570Z = -1.8912$$

where X, Y, and Z are the coordinates (in Å) referring to the orthogonal axes a, b, and c, respectively. Shift of the zinc ion from this plane is significant, as is listed in Table 3 along with those of nine nitrogen atoms. It is obvious that the central zinc ion is displaced from the plane by nearly 0.5 Å presenting a pavilion roof shape, as shown in Fig. 5, which is an edge-on projection of the planar molecule viewed in a direction through two bridge nitrogen atoms, N6 and N8. Details of the coordinating feature around the zinc ion are given in Fig. 6. The Zn ion is displaced from the square nitrogen plane by 0.480 Å holding a bond length of 2.061 Å to the four pyrrole nitrogens on an average, and also that of 2.178 Å from the additive ligand nitrogen N9 toward which the Zn ion is shifted. The direction of the Zn–N9 bond is not perpendicular to the basal nitrogen plane, but slightly tilts towards the α carbon of *n*-hexylamine. Point C_t, the foot of a normal through Zn ion to the basal plane, is regarded as the center of the inner hole of phthalocyanine ring. The mean distance from C_t to the four pyrrole nitrogens is 2.005 Å on an average.

It seems worthwhile to compare the present data with those reported with regard to the five coordinated complexes of various metal derivatives of porphyrin which has the same central configuration as a phthalocyanine molecule. In Table 4, mean lengths and angles are listed for characteristic bonds which were reported concerning α-chlorohemin by Koenig[9] (1965), methoxyiron (III) mesoporphyrin-IX dimethyl ester (MeOFeMeso) by Hoard, Hamor, Hamor and Caughey[10] (1965), monochloroiron tetraphenylporphine (ClFe TPP) by Hoard, Cohen, and Glide[11] (1967) and monoaquozinc (II) tetraphenylporphine (H_2OZn TPP) by Glick, Cohen and Hoard[12] (1967). For comparison the list also includes the corresponding data for phthalocyanine formerly given by Robertson,[13] and its copper and platinum derivatives re-



(a)



(b)

Fig. 4. Bond lengths (a) and inter-bond angles (b). The mean e.s.d. for lengths is about 0.023Å and for angles about 2.1°.

Table 3. Atomic displacements from the mean plane formed by four pyrrole nitrogen atoms

Atom	Shifts
N1	0.008
N2	−0.008
N3	0.008
N4	−0.008
Zn	−0.480
N5	0.181
N6	0.230
N7	0.037
N8	0.046
N9	−2.650

9) D. F. Koenig, *Acta Cryst.*, **18**, 663 (1965).
10) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Amer. Chem. Soc.*, **87**, 2312 (1965).
11) J. L. Hoard, G. H. Cohen, and M. D. Glick, *ibid.*, **89**, 1992 (1967).
12) M. D. Glick, G. H. Cohen, and J. L. Hoard, *ibid.*, **89**, 1966 (1967).
13) J. M. Robertson, *J. Chem. Soc.*, **1936**, 1195. J. M. Robertson and I. Woodward, *ibid.*, **1937**, 219.

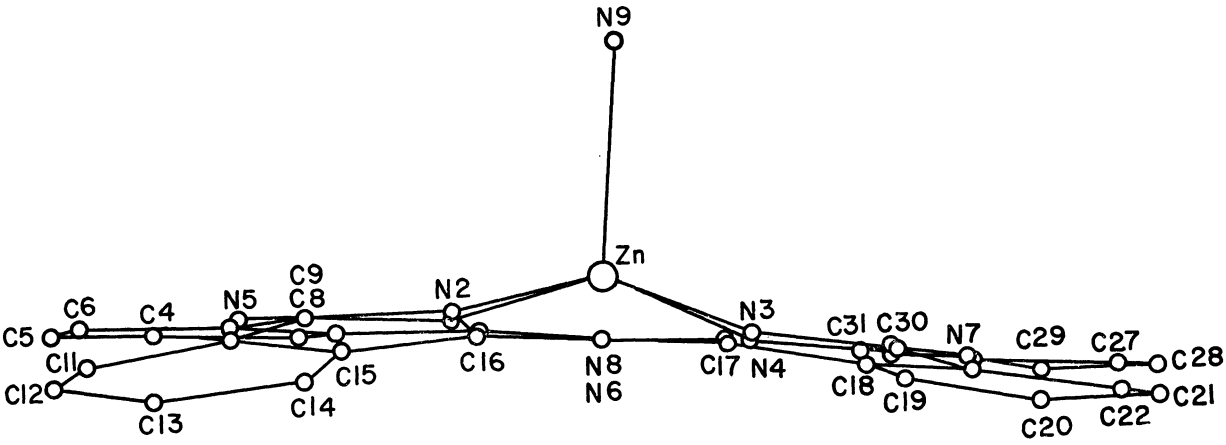


Fig. 5. Edge-on view of the molecule projected perpendicular to the direction through N6 and N8.

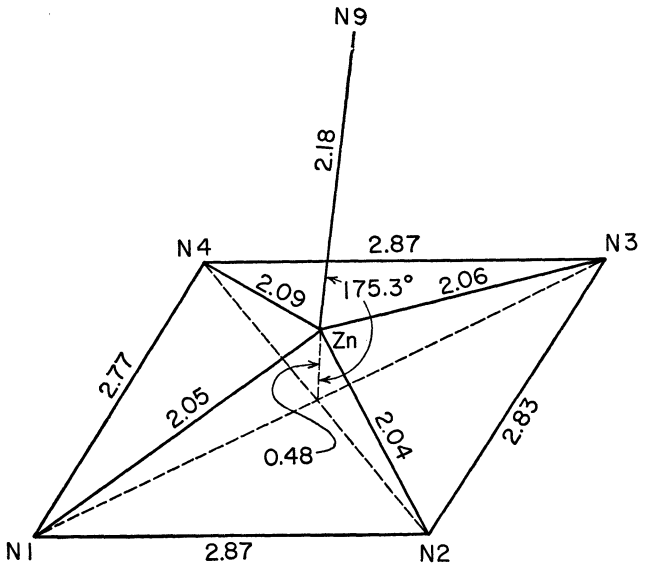


Fig. 6. The square-pyramidal coordinating feature around the zinc ion.

cently determined by Brown.[14,15]

The characteristic bonds are associated with the atoms which are the metal ion (M), the ligand nitrogen coordinated to the metal (N_p), the additive ligand atom (L), the α and β carbon of pyrrole rings (C_α, C_β) and the methin carbon (C_m) or the bridge nitrogen (N_b) both of which connect two adjacent pyrrole rings. Although it is obvious that the corresponding values do not differ much from one another, the zinc phthalocyanine complex shows a closer resemblance to α-chlorohemin than the aquo zinc TPP, particularly in the dimensions of such bonds as M–N_p, C_t–N_p, C_t–M and N_p–C_α, all being associated with the configuration of coordinate systems of the common convex type. A characteristic feature of the porphine skeleton in which the bond N_p–C_α is always longer than the C–C bonds in benzene ring in the case of phthalocyanines also holds in the present complex. The inner hole radius, C_t–N_p, is longer than that of any other phthalocyanine though it is closer to the radii of Pt derivatives of both modifications. It is likely that the complex formation does not affect the bond lengths around the bridge nitrogens. The molecule of phthalocyanine and its metal derivatives is well known as a flat molecule. As an example, the shifts of carbon atoms in copper phthalocyanine crystal from the mean plane were reported by Brown[14] to be within ± 0.05 Å. Every divalent metal ion situated in the center of a phthalocyanine molecule takes a square planar four coordinate structure, where the metal ion bonds with four nitrogens through dsp^2 hybrid orbitals. These square planar configurations are possible for Mn, Fe, Ni, Pd, and the four coordinate square planar configurations are very stable especially for Co, Ni, Cu, Pt ions. The fact that the phthalocyanine derivatives of nickel or copper do not make an additive complex with amines, and manganese derivative reacts with molecules of amine to form a six coordinate complex, suggests that the reactivity of metal phthalocyanine with the various amines depends mostly on the electronic configurations in $3d$ orbitals of metal ion. In other words, manganous and ferrous ion can form six coordinate octahedral configurations with d^2sp^3 hybrid orbitals. The phthalocyanine derivatives of these two metal ions, therefore, can easily form molecular complexes with other ligands such as pyridine, aniline or other amines.

In contrast, divalent zinc ion whose $3d$ electron orbitals are filled with its own ten electrons is apt to take tetrahedral configuration by use of sp^3 hybrid orbitals. The zinc ion uses outer sp^2d hybrid orbitals in order to stay in phthalocyanine ring because the zinc ion is required to assume a square planar coordination which is not a stable configuration for the ion. Thus, zinc phthalocyanine shows a tendency to form a five or six coordinate complex when n-donor molecule exists. In the complex with n-hexylamine, the zinc ion takes a square pyramidal five coordination as shown in Fig. 6. In this case sp^2d^2 hybridized orbitals were used for the coordination. It is interesting to note that the phthalocyanine molecule which is usually considered to have a rigid planner configuration can be easily distorted by complex formation in the crystal.

14) C. J. Brown, *ibid.*, **1968**, 2488.
15) C. J. Brown, *ibid.*, **1968**, 2492.

TABLE 4. THE MEAN LENGTHS AND ANGLES OF CHARACTERISTIC BONDS IN VARIOUS PORPHYRINE DERIVATIVES

Metal Name	Fe α-Cl hemin	Fe Me-O-Fe mesoporph.	Fe Fe-TPP -Cl	Zn Aquo- Zn-TPP	Zn Zn-Phc *n*-hexyl.	Cu Cu-Phc	Ni Ni-Phc	Pt Pt-Phc (α)	Pt Pt-Phc (β)	Free H_2-Phc
C_t-M	0.475	0.455	0.383	0.19	0.48	0	0	0	0	0
C_t-N_p	2.007	2.002	2.012	2.04	2.00	1.935	1.83	1.98	1.98	1.92
M-N_p	2.062	2.073	2.049	2.05	2.06	1.935	1.83	1.98	1.98	1.92
M-L	2.218	1.842	2.129	2.20	2.17					
N_p-C_α	1.38	1.395	1.384	1.38	1.38	1.366	1.39	1.35	1.37	1.34
C_α-C_m (N_b)	1.38	1.377	1.399	1.42	1.34	1.328	1.34	1.33	1.33	1.34
C_α-C_β	1.45	1.446	1.446	1.43	1.47	1.453	1.46	1.49	1.43	1.49
C_β-C_β	1.33	1.368	1.380	1.37	1.43	1.400	1.38	1.37	1.46	1.39
$\angle C_\alpha N_p C_\alpha$	106.1	107	106	105.4	109.3	107.3	99.0	111	109	108.5
$\angle C_m(N_b)$	125.9	124.1		125.9	124.5	122.2	117	120	124	117
Ligand	Cl	O	Cl	O	N					
year	1965	1965	1967	1967	1971	1968	1937	1968	1968	1936
Ref.	8	9	10	11	this paper	13	12	14	14	12

Another example of five coordinate zinc ion can be seen in the molecule of aquozinc tetraphenyl porphine, where zinc ion takes a square-pyramidal structure although copper or palladium derivatives show a square-planar structure without any water molecule coordinated to them. In this case, bond distances of Zn–N and Zn–O are 2.05±0.01 Å and 2.20±0.06 Å, respectively, and in the case of zinc phthalocyanine-*n*-hexylamine complex the bond lengths of Zn–N and Zn–N (amine) are 2.06±0.02 Å and 2.18±0.02 Å. These similarities indicate that the zinc ions in both complexes take the same electronic configuration by sp^2d^2 orbitals for coordinations which seems more stable than the square planar structure of sp^2d orbitals. The paired molecules viewed in a direction perpendicular to the molecular plane shows that the intermolecular overlapping area is very small. In general, the packing manner in the crystals of the planar molecules like phthalocyanines is said to be stable when the overlap of π-electron is made as large as possible. Judging from these facts the small overlap of the pair of planar molecules may suggest the change of distributions of π-electron density in phthalocyanine molecules due to the charge transfer from amine to phthalocyanine ring.

The number of *n*-hexylamine molecules which exist in a unit cell of the complex was determined by means of differential thermal analysis (DTA) and thermal gravimetric analysis (TGA). There are three endothermic reactions at about 140, 155, and 180°C.

The first reaction detected at 140°C by DTA is related to the partial decomposition of the complex. When the amines have been released by decomposition, they are usually discharged instantly into the air. The endothermic reaction at 155°C is related to the evaporation of these discharged hexylamines at boiling point. Though the boiling point of *n*-hexylamine is 130°C, it is detected as a peak temperature at 155°C by DTA when the rate of temperature rise is 10°C/min. The last peak was attributed to the decomposition and evaporation of the *n*-hexylamine tightly bonded to zinc phthalocyanine. It should be emphasized that there are two bonding states for *n*-hexylamine in the complex crystal. One is weakly bonded and can be easily released from the lattice at a temperature lower than the boiling point of *n*-hexylamine. The other is strongly bonded and stable up to about 180°C. It is evident from TGA that the total number of *n*-hexylamine in a unit cell is six where as that of zinc-phthalocyanine is four. The electron density map obtained by Fourier synthesis gave only four *n*-hexylamine molecules coordinated directly to the zinc ion in a unit cell. The other two amine molecules did not appear in the course of the Fourier synthesis. These molecules are considered to be located at random in a space of crystal lattices and discharged out of the lattice even at low temperature. The coordinated *n*-hexylamine molecules are considered to be more stable so as to be decomposed at about 180°C. None of the atomic parameters of these coordinated amines except the nitrogen were exactly determined and the electron densities of five carbon atoms of the amine were only about 1/3-1/5 of the density of the carbons in phthalocyanine ring at the final stage of refinement. No terminal methyl carbon of the *n*-hexylamine was detected. The indistinctness of the atomic parameters was due to a molecular rotation or a static disorder of the paraffine chain of the amine. A preliminary structural study on a series of similar additive complexes shows that the crystals of such molecular complexes of zinc phthalocyanine with normal amine, whose carbon numbers are three, four, and five have an isomorphous structure with the complex reported here. It is observed that thermal stability decreases with the decrease of the carbon number of amine. In the case of the complex with propylamine (C=3) the weakly bonded amine in the crystal lattice easily escapes from the lattice even at room temperature leaving 1 : 1 complex behind. It may be possible to determine the position of all the atoms of amine in the crystal by means of low temperature Weisenberg camera because the quenching of the movement of amine molecule can be expected.