

## Crystal and Molecular Structures of Bisphthalocyaninatothorium (IV)

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Bisphthalocyaninatothorium(IV),  $(C_{32}N_8H_{16})_2Th$ , structure was studied by three dimensional x-ray analysis. The crystal belongs to a space group  $C2/c$  with the cell dimensions  $a=18.92$ ,  $b=18.81$ ,  $c=15.92$ , and  $\beta=116^\circ$ . Two phthalocyanine ligands are linked by one thorium ion to form a sandwich-like molecule.

The parallel mean planes of the ligands are separated by 3.59Å. The thorium ion is displaced 1.49Å from the plane of pyrrole nitrogens.

### INTRODUCTION

Phthalocyanine ligand,  $(C_{32}N_8H_{16})^{--}$ , Pc, forms easily metal complex with most of divalent metal ions. X-ray studies revealed that the divalent metal derivatives are mostly plane molecules.<sup>1)</sup> The metal ion is placed in the molecular center and has a coordination number 4. Sn(II)<sup>2)</sup> and Pb-Pcs<sup>3)</sup> are the exceptions.  $Sn^{2+}$  and  $Pb^{2+}$  are forced out from the molecular plane. When a monovalent ligand such as  $Cl^-$ ,  $OH^-$ , and other molecule with lone pair electrons, is attached to the metal ion in the molecule, the ligand pulls out the metal ion from the molecular plane of Pc ligand and makes a square pyramidal structure.<sup>4)</sup> The metal ion has a coordination number 5 in this case and the Pc ligand deforms and loses its flatness.<sup>5)</sup> Recently it has been reported<sup>6,7)</sup> that tetrapositive metal ions, U(IV) and Sn(IV), form eight coordinate complex with two Pc ligands. In such complexes the metal ions are located between two ligands. U- and Sn-Pc<sub>2</sub> differ in their crystal structures from each others. The present investigation is to determine the crystal and molecular structures of Th-Pc<sub>2</sub>. The deformation of Pc ligand and the bonding configuration of the thorium ion are also of interest from the view point of intermolecular forces.

### EXPERIMENTAL

Th-Pc<sub>2</sub> was obtained by direct reaction of thorium metal powder and *o*-phthalodinitrile at about 270°C and purified by sublimation in reduced nitrogen gas flow at 600°C in a silica tube. The thorium powder was washed by dilute chloric acid before the reaction. Parallelepiped crystals were obtained and identified with chemical analysis as  $(C_{32}N_8H_{16})_2Th$ . Calculated: C: 61.15 % N: 17.83 % H: 2.56 %.

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Observed: C: 61.45 % N: 18.00 % H: 2.8 %. Equi-inclination Weissenberg photographs about c- and b-axis were taken for a crystal of  $0.1 \times 0.5 \times 0.2$  mm by the use of Ni-filtered Cu-K $\alpha$  radiation. Intensities of 3500 independent reflections were measured visually.

No correction was made for absorption. Atomic scattering factors for Th<sup>4+</sup> were taken from Ref.11.

### RESULTS AND DISCUSSIONS

The crystal is monoclinic and belongs to a space group C2/c. The cell constants are  $a=18.92 \pm 0.01$ ,  $b=18.81 \pm 0.01$ ,  $c=15.92 \pm 0.01$  and  $\beta=116^\circ$ . The measured density by floatation method is  $1.66 \text{ g/cm}^3$  and the calculated is  $1.640 \text{ g/cm}^3$ . Each unit cell has four molecules and no extra extinction was observed in reflections. Therefore, it is decided that the centers of the molecules are on the crystallographic two fold axes at  $(0.0, y, 0.25)$ ,  $(0.0, y, 0.75)$ ,  $(0.5, y+0.5, 0.25)$  and  $(0.5, 0.5+y, 0.75)$  which are parallel to the b-axis. The y-coordinate was obtained from a Patterson synthesis. A Fourier map exhibited the positions of all carbon and nitrogen atoms. The final parameters refined repeatedly through a full-matrix least-squares method are listed in Table I. The final R-value was 0.12. Figure 1 shows the projection of molecular arrangement in the crystal along the b-axis schematically. The bond distances and angles in an asymmetrical unit are given in Fig. 3. One molecule consists of a thorium ion and two Pc ligands. Thorium ion has a coordination number 8 and is located at the center of molecule. The center is 1.49Å apart from the plane defined by four pyrrole nitrogen atoms(N1-N4). The bond lengths between the nitrogen and thorium are 2.482Å on the average. The length is slightly longer than the corresponding length in U- and Sn-Pc<sub>2</sub> which were reported to have similar molecular structures to the present one. The four pyrrole nitrogen atoms form a plane represented by the following least-squares equation,

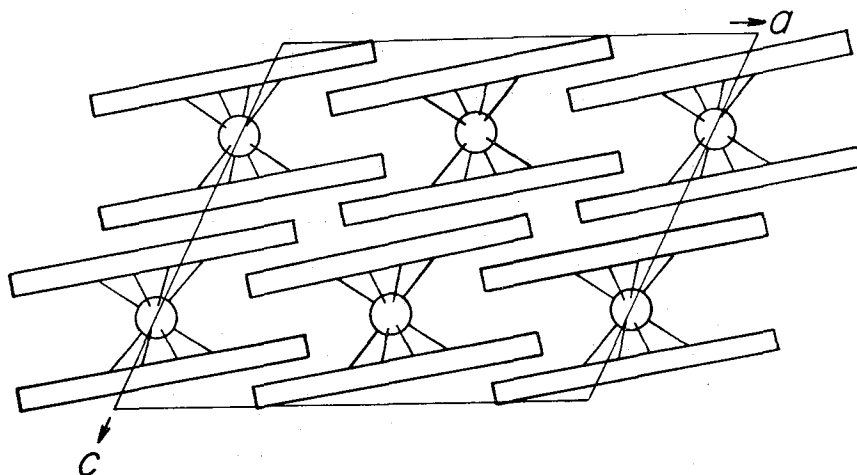


Fig. 1. Diagrammatic projection along b-axis showing the relative orientation of the phthalocyanine ligands and thorium ion.

### Crystal Structure of Bisphthalocyaninatothorium

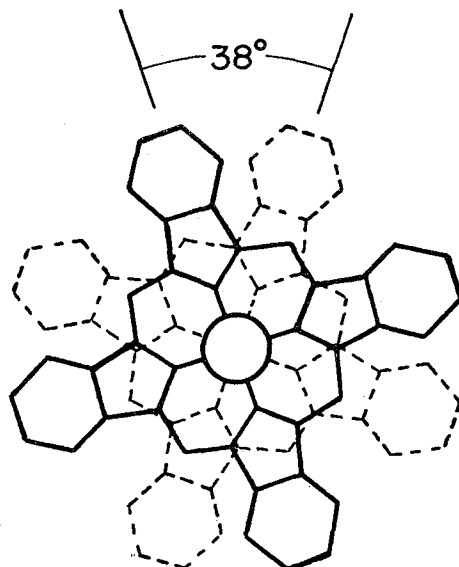


Fig. 2. Projection of the molecule onto the plane defined by four pyrrole nitrogen atoms ( $N_p$  square plane).

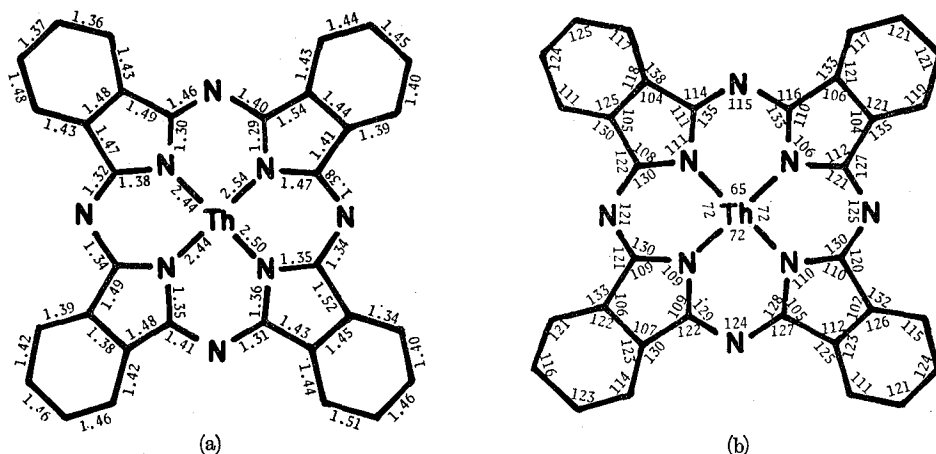


Fig. 3. Bond lengths (a) and angles (b) in an asymmetrical unit.

$$0.1857X - 0.030Y + 0.9821Z - 1.5095 = 0 \text{ (Plane 2)}$$

where X, Y, and Z are the coordinates (in Å) referring to the orthogonal axes a, b, and c respectively. Displacements of the atoms of the molecule from this plane are listed in Table II. Two pyrrole nitrogen planes, which are confronted with each other and between which a thorium ion is situated, are separated by 2.98 Å. The separation is larger than those of U- and Sn-Pc<sub>2</sub> (2.81 Å and 2.70 Å). This fact suggests that the ionic radius of thorium ion is larger than those of uranium or tin tetrapositive ions.

The mean least-squares plane defined by all carbon and nitrogen atoms in a ligand

Table I. Atomic and Thermal Parameters

ATOM	X	Y	Z	B <sub>11</sub> OR B
TH	0.0	0.41691	0.25000	*
N 1	0.04492	0.45113	0.12648	3.585
N 2	-0.07789	0.51854	0.16285	2.818
N 3	-0.13895	0.38382	0.17477	3.309
N 4	-0.01496	0.31687	0.14010	3.749
N 5	0.01943	0.58004	0.11632	7.680
N 6	-0.19920	0.49864	0.17848	3.640
N 7	-0.12877	0.25513	0.14713	3.537
N 8	0.09597	0.33535	0.10329	3.319
C 1	0.09714	0.40861	0.10022	3.325
C 2	0.15018	0.45144	0.08210	3.750
C 3	0.21444	0.43785	0.06361	3.401
C 4	0.25408	0.49464	0.04707	4.577
C 5	0.22700	0.56692	0.04441	3.998
C 6	0.18038	0.58210	0.06218	4.267
C 7	0.12399	0.52321	0.08426	3.322
C 8	0.05440	0.51643	0.10906	2.607
C 9	-0.04776	0.57159	0.13745	3.187
C10	-0.08993	0.63886	0.13528	3.485
C11	-0.08543	0.71239	0.11526	4.892
C12	-0.14375	0.75557	0.11383	4.665
C13	-0.20380	0.73470	0.13426	5.779
C14	-0.21381	0.66119	0.15960	5.590
C15	-0.15296	0.61598	0.16061	3.131
C16	-0.14602	0.53821	0.16799	2.915
C17	-0.19720	0.42757	0.17356	2.550
C18	-0.26602	0.38339	0.16250	3.940
C19	-0.33821	0.39992	0.16121	6.458
C20	-0.39475	0.34610	0.14852	7.632
C21	-0.37306	0.27390	0.13547	7.816
C22	-0.29747	0.25592	0.13677	5.418
C23	-0.24573	0.31426	0.15389	4.639
C24	-0.16531	0.31632	0.16113	3.684
C25	-0.06390	0.25594	0.13711	3.696
C26	-0.02424	0.19556	0.12295	3.799
C27	-0.05228	0.12329	0.11405	6.391
C28	-0.00349	0.07415	0.08546	8.149
C29	0.06419	0.10054	0.07376	6.761
C30	0.08624	0.17224	0.08225	5.091
C31	0.03872	0.21647	0.09971	4.469
C32	0.04161	0.29668	0.11466	2.251

\* The anisotropic temperature factor for thorium ion is defined by the expression,

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

$$\beta_{11}=0.0016, \beta_{22}=0.0013, \beta_{33}=0.0059,$$

$$\beta_{12}=0.0000, \beta_{23}=0.0000, \beta_{13}=0.0032.$$

Crystal Structure of Bisphthalocyaninatothorium

Table II. Displacements of Atoms from the Mean Least-Squares Planes of Plane 1 (All Carbon and Nitrogen Atoms), Plane 2 (Pyrrole Nitrogens) and Plane 3 (Bridge Nitrogen Atoms N5-N8)

$$\text{Plane 1. } -0.1225X - 0.0160Y - 0.9923Z + 1.6670 = 0$$

$$\text{Plane 2. } -0.1857X + 0.0307Y - 0.9821Z + 1.5100 = 0$$

$$\text{Plane 3. } -0.1667X + 0.0074Y - 0.9860Z + 1.5427 = 0$$

Plane 1		Plane 2		Plane 3	
ATOM	SHIFT	ATOM	SHIFT	ATOM	SHIFT
N 1	-0.2698	N 1	-0.0095	N 5	0.0595
N 2	-0.4782	N 2	0.0090	N 6	-0.0720
N 3	-0.4585	N 3	-0.0092	N 7	0.0791
N 4	-0.2101	N 4	0.0099	N 8	-0.0561
N 5	-0.1017	N 5	0.2958	N 1	-0.1821
N 6	-0.4051	N 6	0.2193	N 2	-0.2441
N 7	-0.0752	N 7	0.2320	N 3	-0.2277
N 8	-0.0405	N 8	0.0428	N 4	-0.1274
C 1	-0.0248	C 1	0.1197	C 1	-0.0104
C 2	0.0864	C 2	0.1940	C 2	0.0679
C 3	0.1849	C 3	0.1932	C 3	0.0995
C 4	0.2994	C 4	0.3004	C 4	0.1993
C 5	0.3758	C 5	0.4711	C 5	0.3290
C 6	0.2858	C 6	0.4849	C 6	0.3087
C 7	0.0926	C 7	0.2966	C 7	0.1289
C 8	-0.0754	C 8	0.2203	C 8	0.0257
C 9	-0.2155	C 9	0.2679	C 9	0.0069
C10	-0.1188	C10	0.4722	C10	0.1671
C11	0.1086	C11	0.7472	C11	0.4152
C12	0.2521	C12	0.9977	C12	0.6259
C13	0.1307	C13	0.9419	C13	0.5537
C14	-0.1678	C14	0.6057	C14	0.2414
C15	-0.3041	C15	0.3575	C15	0.0348
C16	-0.3954	C16	0.1937	C16	-0.0937
C17	-0.3230	C17	0.2337	C17	-0.0247
C18	-0.0046	C18	0.5889	C18	0.3271
C19	0.3156	C19	1.0038	C19	0.7107
C20	0.5019	C20	1.2088	C20	0.9195
C21	0.6442	C21	1.2539	C21	1.0066
C22	0.4575	C22	0.9611	C22	0.7489
C23	0.0871	C23	0.5904	C23	0.3680
C24	-0.1933	C24	0.2197	C24	0.0240
C25	-0.0835	C25	0.1415	C25	0.0133
C26	0.0847	C26	0.1962	C26	0.1131
C27	0.2494	C27	0.3295	C27	0.2683
C28	0.4289	C28	0.3941	C28	0.3765
C29	0.5030	C29	0.4000	C29	0.3985
C30	0.3219	C30	0.2602	C30	0.2337
C31	0.1718	C31	0.2160	C31	0.1497
C32	-0.0531	C32	0.0682	C32	-0.0356
TH	-1.7950	TH	-1.4390	TH	-1.6359

is given by the equation,

$$0.1225X + 0.0160Y + 0.9923Z - 1.6670 = 0 \text{ (Plane 1).}$$

Comparing the atomic displacements from this plane shown in Table II with the values of 0.03A in the  $\beta$ -form copper-Pc and of 0.05A in  $\gamma$ -form platinum-Pc, the deformation of Th-Pc<sub>2</sub> is predominant.

Equation representing the plane of four outer nitrogen atoms (N5-N8) in thorium derivative in reference to the standard orthogonal axes is

$$0.1667X - 0.0074Y + 0.9860Z - 1.5427 = 0 \text{ (Plane 3).}$$

The displacement of carbon atom from this plane is 0.92 A in the maximum. The inner four nitrogen (pyrrol) atoms are separated by 0.15A from this plane. The isoindole rings make dihedral angles of 6–15° with respect to this plane. Planes of four isoindole rings and dihedral angles between the least-squares planes are also given in Table III and Table IV with the deviations of atoms from the planes.

The distances between two parallel planes of pyrrole nitrogens in the tetrapositive metal derivatives are shorter than 3.354 A interlayer spacing of graphite and 3.34 A intermolecular distance in  $\beta$ -form Cu-Pc. Intermolecular distances in aromatic crystals are usually longer than the interlayer distance of graphite. The shorter length of  $\beta$ -form copper-Pc than this distance is considered to be due to a strong intermolecular force like a charge transfer force. However even in the well known T.C.N.Q.-T.T.F. charge transfer complex<sup>8)</sup> with strong charge transfer interactions among the molecules, the intermolecular distance is 3.17 A. When aromatic molecules come nearer than this distance, some repulsive forces act to separate the molecules. Therefore the outer parts of the ligands in Th-Pc<sub>2</sub> bend back opposite in order to

Table III. The planes of Four Isoindole Rings and the Displacement of the Atoms From the Planes

Plane 4.		Plane 5.		Plane 6.		Plane 7.	
ATOM	SHIFT	ATOM	SHIFT	ATOM	SHIFT	ATOM	SHIFT
N 1	-0.0804	N 2	-0.0161	N 3	-0.0176	N 4	-0.0186
C 1	0.0884	C 9	0.0471	C17	0.0016	C25	0.0256
C 2	0.0270	C10	-0.0243	C18	-0.0273	C26	-0.0215
C 3	0.0004	C11	-0.0318	C19	0.0728	C27	0.0052
C 4	-0.0465	C12	0.0286	C20	-0.0759	C28	-0.0160
C 5	-0.0086	C13	0.0315	C21	-0.0017	C29	0.0200
C 6	0.0292	C14	-0.0232	C22	0.0530	C30	-0.0111
C 7	-0.0000	C15	-0.0737	C23	-0.0087	C31	0.0202
C 8	-0.0027	C16	0.0660	C24	0.0107	C32	-0.0013
TH	-1.3544	TH	-1.0394	TH	-0.8537	TH	-1.2990

Crystal Structure of Bisphthalocyaninatothorium

Table IV. Dihedral Angles Between the Planes in Table II and III.

BETWEEN THE PLANES 1 AND 2	4.55 DEGREE
BETWEEN THE PLANES 1 AND 3	2.89 DEGREE
BETWEEN THE PLANES 1 AND 4	7.00 DEGREE
BETWEEN THE PLANES 1 AND 5	9.53 DEGREE
BETWEEN THE PLANES 1 AND 6	13.52 DEGREE
BETWEEN THE PLANES 1 AND 7	8.44 DEGREE
BETWEEN THE PLANES 2 AND 3	1.74 DEGREE
BETWEEN THE PLANES 2 AND 4	6.77 DEGREE
BETWEEN THE PLANES 2 AND 5	11.88 DEGREE
BETWEEN THE PLANES 2 AND 6	15.78 DEGREE
BETWEEN THE PLANES 2 AND 7	4.71 DEGREE
BETWEEN THE PLANES 3 AND 4	6.07 DEGREE
BETWEEN THE PLANES 3 AND 5	10.50 DEGREE
BETWEEN THE PLANES 3 AND 6	15.18 DEGREE
BETWEEN THE PLANES 3 AND 7	6.23 DEGREE
BETWEEN THE PLANES 4 AND 5	6.37 DEGREE
BETWEEN THE PLANES 4 AND 6	20.51 DEGREE
BETWEEN THE PLANES 4 AND 7	11.21 DEGREE
BETWEEN THE PLANES 5 AND 6	21.54 DEGREE
BETWEEN THE PLANES 5 AND 7	16.59 DEGREE
BETWEEN THE PLANES 6 AND 7	15.54 DEGREE

reduce the repulsive forces between two planes. As a result the Pc ligands deform and become saucer-shape.

Figure 2 shows the relative orientation of two Pc ligands which are related to each other by two-fold axis. The axis passes through the central thorium ion and parallel to the crystal b-axis. The staggering angle of the Pc rings is  $38^\circ$ . The angle in Sn(IV)- and U(IV)-Pc<sub>2</sub> are  $42^\circ$  and  $37^\circ$  respectively (Table IV). In the case of phthalocyanato-pyridine-manganese(III)- $\mu$ -oxo-phthalocyanato-pyridine-manganese(III)-di-pyridine<sup>9</sup> which consists of two Pc ring systems having a manganese ion of coordination number 6 at the center of each Pc ligand, and of four pyridine molecules, the staggering angle is  $49^\circ$  as reported by Vogt *et. al.* The angle was interpreted in terms of molecular interaction between the coordinated pyridine molecules. In this complex two Pcs are linked together by one oxygen atom between them through single bonds. They are able to rotate freely around the bonds and the intermolecular forces of surrounding molecules can determine the positional correlation of the two Pcs. The Pc ligands are separated 3.42 Å which is longer than the intermolecular distance of square planar manganese(II)-Pc (3.18 Å).<sup>10</sup> On the contrary in the tetrapositive metal phthalocyanines, two ligands are forced to be definitely linked by eight coordinate bonds between the ion and ligands. There are various factors to determine the positional correlation between two Pc ligands. The shape of the hybridized electron orbitals of the metal ions and their ionic radii should be one of the factors. The other factor is repulsive force acting between two ligands. As

Table V. Comparison of Th-, U-, and Sn-Pc<sub>2</sub>. The Bond Length and Angles are Averaged for Chemically Equivalent Values

		Th-Pc <sub>2</sub>	U-Pc <sub>2</sub>	Sn-Pc <sub>2</sub>
Crystal data				
Space group		C2/c	C2/c	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a		18.92	18.74	10.55 (Å)
b		18.81	18.73	50.74
c		15.92	15.61	8.90
$\beta$		116.0	113.6	90.0 (deg)
V		5092	5020	4764 (Å <sup>3</sup> )
Z		4	4	4
$\rho$		1.64	1.67	1.60 (g/cm <sup>3</sup> )
Averaged bond distances				
Pyrrole ring	N <sub>p</sub> -C	1.37	1.38	1.38 (Å)
	C-C	1.48	1.46	1.47
Pyrrole pyrrole link	C-N <sub>b</sub>	1.37	1.32	1.32
Phenyl pyrrole	C-C	1.44	1.40	1.39
Phenyl	C-C	1.41	1.40	1.41
	C-C	1.43	1.39	1.41
	C-C	1.43	1.41	1.42
Averaged bond angles				
Pyrrole ring	C-N <sub>p</sub> -C	109.2	107.9	108.1 (deg)
	N <sub>p</sub> -C-C	109.4	109.4	109.2
	C-C-C	105.6	106.6	106.6
Pyrrole pyrrole	N <sub>p</sub> -C-N <sub>b</sub>	129.4	127.6	128.7
	C-C-N <sub>b</sub>	121.1	123.0	121.8
	C-N <sub>b</sub> -C	121.2	123.9	121.3
Pyrrole phenyl	C-C-C	131.8	131.8	130.5
	C-C-C	122.3	121.6	122.7
Phenyl ring	C-C-C	115.7	116.8	155.3
	C-C-C	121.8	121.5	121.8
Metal-N <sub>p</sub> distance		2.48	2.43	2.35 (Å)
Distance of metal to N <sub>p</sub> square plane		1.49	1.40	1.35
Size of N <sub>p</sub> square plane		2.87	2.80	2.766
Distance between two N <sub>p</sub> square planes		2.98	2.81	2.70
Rotation of phthalocyanine rings		38	37	42 (deg)

mentioned above, the inner parts of Pc rings in Th-Pc<sub>2</sub> come to each other closer than van der Waals distances of aromatic ring molecules. This fact suggests that the repulsive forces between them should have some important influence on determining the molecular configuration. The packing relations of the molecules in crystal also affect to some extent and the combination of these factors and other unknown factors results in the molecular structures presented here. The first factor is the most effective, therefore thorium and uranium ions, both of which belong to the actinide elements and have the similar electron configurations, form the isomorphous phthalocyanine complexes while stannic Pc has a different molecular and crystal structures.



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