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Crystal and Molecular Structures of Two Phthalocyanines, Chloro(phthalocyaninato)gallium(III) (ClGaPc) and μ -Oxobis(phthalocyaninato)gallium(III) (PcGaOGaPc)

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Abstract: The structure of μ -oxobis(phthalocyaninato)gallium(III) (PcGaOGaPc) and the structure of a second modification of chloro(phthalocyaninato)gallium(III) (ClGaPc) has been determined by single-crystal X-ray analysis. Sublimation of the respective compounds led to single crystals suitable for an X-ray study. Both compounds crystallize in the triclinic space group $P\bar{1}$, with a unit cell for ClGaPc $a = 13.770 \text{ \AA}$, $b = 13.770 \text{ \AA}$, $c = 14.039 \text{ \AA}$, $\alpha = 98.32^\circ$, $\beta = 108.64^\circ$, $\gamma = 90.01^\circ$, containing four disordered molecules ($Z = 4$). The unit cell of the dimeric PcGaOGaPc contains one molecule, with half a molecule as an asymmetric moiety ($Z = 2$) and $a = 7.848 \text{ \AA}$, $b = 12.529 \text{ \AA}$, $c = 12.720 \text{ \AA}$, $\alpha = 91.03^\circ$, $\beta = 94.94^\circ$, $\gamma = 89.98^\circ$. The Ga atoms for the two ClGaPc molecules are placed $0.44 \text{ \AA}$ above the plane formed by the respective isoindole nitrogen N1 to N4. The two rings of the asymmetric unit (molecule 1 and 2) are arranged in parallel, with ca. $3.4 \text{ \AA}$ distance within the unit cell. The Ga-Cl bond distances are ca. $2.20 \text{ \AA}$ for the two molecules. The gallium of PcGaOGaPc is placed $0.49 \text{ \AA}$ above the respective isoindole nitrogen plane and the Ga-O bond amounts to $1.734 \text{ \AA}$.

Keywords: phthalocyanines; gallium compounds; crystal structure; disorder; photosensitivity



Citation: Zugenmaier, P. Crystal and Molecular Structures of Two Phthalocyanines, Chloro(phthalocyaninato)gallium(III) (ClGaPc) and μ -Oxobis(phthalocyaninato)gallium(III) (PcGaOGaPc). *Crystals* **2024**, *14*, 182. <https://doi.org/10.3390/cryst14020182>

Academic Editors: Simona Nica and Pedro Netto Batalha

Received: 31 December 2023

Revised: 31 January 2024

Accepted: 3 February 2024

Published: 12 February 2024



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1. Introduction

Phthalocyanines (Pc) and their derivatives exhibit a variety of useful applications depending on the chemical constitution of the molecule and the crystal structure, as well as on the structural polymorphism when the same chemical constitution is present [1–10]. An excellent tool for the determination of the molecular and crystal structures of these compounds is X-ray single-crystal studies, which reveal the arrangements and interactions that are needed within the materials for applications as active materials for organic electronics, xerography, sensors, photovoltaic cells, electrochromic devices, nonlinear optics, and recordable DVDs.

Structural determination using X-ray powder patterns of randomly distributed crystallites that all exhibit the same structure is difficult and can only be successful with an additional conformation and packing analysis for the Pcs with an almost firm conformation of the molecules to substitute the few available X-ray data. But this method can serve as an approximation only. Nevertheless, single-crystal data are still needed as prerequisites for such an investigation to supplement the missing data as the molecular conformation or as bond lengths and angles. Such a structural determination by an X-ray powder experiment was carried out to refine the structure of HOGaPc V [2], starting with the isomorphous unit cell of TiOPc II or VOPc II and a fixed conformation of the HOGaPc molecule. The conformation was obtained by single-crystal analysis for these two compounds [11]. The replacement of the central atoms, Ti or V, by Ga in the fixed conformation of TiOPc or VOPc slightly changed the packing arrangement of the HOGaPc V structure due to small differences in the size of the unit cells considered. Since the size of the unit cells is established by the interactions of all atoms, the few interactions with the central atoms, Ga, O, Ti or V, in the packing refinement can be neglected compared with the many interactions of all the

other atoms of the Pc molecule, which all contribute to the total energy. This method of neglecting small contributions to the total energy was introduced in the structural calculations of monosaccharides by neglecting hydrogen bonds [12]. A packing analysis with few variables then leads to an excellent approximation of the of HOGaPc V structure. The central atoms can then be determined with the few reflections available by an X-ray analysis of the powder pattern.

The relationship between crystal structure and photosensitivity of Pc polymorphs is described by Oka and Okada [1]. The photosensitivity is caused by a certain overlap in the stacking of adjacent molecules, alongside the separation distance of the two molecules, allowing π -interactions, which was found to be optimal for HOGaPc V and high photosensitivity is the result.

X-ray powder diagrams without any relation to structural features are used to characterize properties of phthalocyanines, especially in the patent literature, without a detailed knowledge of the interactions of the molecules responsible for the proposed properties. It is sometimes rather difficult to obtain an accurate structure with powder X-ray data, or at least a reliable unit cell as prerequisite for a crystal structure determination. An interpretation of powder X-ray data is, in many cases, not trustworthy. Therefore, a single-crystal structure evaluation by X-ray analysis, as carried out for PcGaOGaPc and ClGaPc, is still an elegant way to obtain the required structures for a discussion of properties. However, this method requires special crystallization procedures to obtain the needed crystals. Single-crystal analysis can also provide the required geometrical data and interaction parameters for phthalocyanines to compare with results obtained by other methods, i.e., by spectroscopy, such as X-ray absorption spectroscopy (EXAFS [9]), or by theoretical quantum chemical studies [10].

2. Materials and Methods

Single crystals of chloro(phthalocyaninato)gallium(III) (ClGaPc) and μ -oxo-bis(phthalocyaninato)gallium(III) (PcGaOGaPc) suitable for a single-crystal X-ray analysis were achieved by sublimation of these compounds. However, it was difficult to find proper materials for the ClGaPc investigations. The results obtained from the evaluation of the X-ray data looked different for various samples from the same batch. Two of these investigations have been included in the discussion of the results, presented as solution a, b, with a maximum scattering angle of $\theta = 20^\circ$ for a and 23° for b. The X-ray data have been collected with a CAD4 Enraf-Nonius single-crystal diffractometer at $T = 291(2)$ K and are summarized in Table 1. The intensities of the reflections were then processed with the MolEN package [13] on a Micro VAX computer and the structures determined by direct methods [14] and refined [15,16] on a personal computer. Hydrogen atoms were placed at respective positions and refined for PcGaOGaPc but not for ClGaPc. The figures describing the structures were produced with the SCHAKAL99 program [17] and Ortep3 [18]. The molecular structure and packing arrangements of the two distinct Pcs will be discussed and compared with the two isomorphous AlPcs [19,20] and a related Ga-Pc compound.

Table 1. Crystallographic data for the dimer PcGaOGaPc and a second modification of ClGaPc with two different solutions a, b.

Compound	$(\mu\text{-Oxo})\text{bis}[(\text{phthalocyaninato})\text{gallium(III)}]\text{GaO}_{0.5}\text{Pc}$	Chloro(phthalocyaninato)gallium(III) ClGaPc	
		Solution a	Solution b
Molecular formula	C ₃₂ H ₁₆ Ga, N ₈ , O _{0.5}	C ₃₂ H ₁₆ Cl, Ga, N ₈	
Formula weight [g/mol]	590.25	617.70	
Crystal system	triclinic	triclinic	
Space group	$P\bar{1}$	$P\bar{1}$	

Table 1. Cont.

Compound	$(\mu\text{-Oxo})\text{bis}[(\text{phthalocyaninato})\text{gallium(III)}]\text{GaO}_{0.5}\text{Pc}$	Chloro(phthalocyaninato)gallium(III) ClGaPc	
		Solution a	Solution b
a [Å]	7.848(2)	13.770(3)	13.772(3)
b [Å]	12.529(3)	13.770(5)	13.766(3)
c [Å]	12.720(3)	14.039(5)	14.038(3)
A [°]	91.03(2)	98.32(2)	98.35(1)
B [°]	94.94(2)	108.64(2)	108.72(1)
γ [°]	89.98(2)	90.01(2)	90.00(2)
V [Å ³]	1245.9(5)	2492.7(14)	2490.8(9)
Z	2	4	
D _{cal} [g/cm ³]	1.573	1.646	1.647
$\mu(\text{MoK}\alpha)$ [mm ^{−1}]	1.148	1.254	1.255
$\lambda(\text{MoK}\alpha)$ [Å]	0.71073	0.71073	
Number of reflections	25	25	25
Scan range in q [°]	13–22	9–20	12–20
Reflections collected	3336	4944	7240
Unique data	3059	4683	6893
Data collection [$<q<$]	1–22	1.5–20.1	1.5–23.1
$I > 2\sigma(I)$	2605	3271	4619
Parameters refined	376	758	758
F(000)	598	1248	
R	0.030	0.044	0.060
R _w	0.075	0.131	0.155
Highest peak [e/Å ³]	0.49	0.54	1.21
Crystal color	dark blue	dark blue	
Crystal size [mm ³]	0.50 × 0.18 × 0.11	0.45 × 0.40 × 0.12	0.50 × 0.35 × 0.15

(Crystallography Open Database) COD 300042, 300483, 300484 contains the supplementary crystallographic data for this paper.

These data can be obtained free of charge via <http://www.crystallography.net/cod/search.html> (accessed on 30 December 2023).

3. Results and Discussions

The positional and averaged thermal parameters for PcGaOGaPc and ClGaPc are collected in Tables A1–A3 in the Appendix A, the respective conformations, thermal ellipsoids with a probability of 50%, and labeling of the atoms are shown in Figures 1 and 2 [18]. In Tables 2 and 3, some selected bond lengths are listed for a comparison of Pc structures. The two Ga-Pc structures investigated are isomorphous with the ones with a central Al atom studied and discussed by Wynne [19,20], space group P-1, with unit cell parameters for PcAlOAlPc of $a = 7.694$ (2) Å, $b = 12.520$ (3) Å, $c = 12.705$ (3) Å, $\alpha = 91.03$ (2)°, $\beta = 94.54$ (2)°, $\gamma = 90.37$ (2)°, and $V = 1219.8$ Å³, and for ClAlPc, $a = 13.776$ (6) Å, $b = 13.775$ (4) Å, $c = 14.059$ (5) Å, $\alpha = 98.36$ (3)°, $\beta = 108.60$ (3)°, $\gamma = 90.16$ (3)°; $V = 2498.2$ Å³. The two unit cells by Wynne agree almost perfectly with the ones listed in Table 1. The packing for the PcGaOGaPc and PcAlOAlPc molecules agrees well (Table A1 and COD 3000042 -file) and can serve as proof that the unit cells are determined by the total interactions of the atoms in

the molecules neglecting the interactions of the central atoms. Wynne had difficulties in solving the structure of ClAlPc and was only able to present one complete molecule of the two in the asymmetric unit. He described the second one as two halves with uncertainties, with a high R factor of 0.137 for 2165 reflections and $I > 3\sigma(I)$ of the 9454 unique reflections in a θ range of $2.8\text{--}140^\circ$ (CuK α) and concluded that limited observed data were obtained as result of disorder in this structure. The highest peak in his difference Fourier amounted to $1.01\text{ e}/\text{\AA}^3$. Due to the perfect agreement of the unit cell with ClGaPc of Table 1, the same arrangement as for ClGaPc can be assumed as listed in Table A2. A structure for ClAlPc can be proposed with the coordinates of ClGaPc without the central atoms. These can be introduced by a refinement with few X-ray data. As suggested, the data of the two GaPc structures may also serve as models for conformations needed for X ray investigations of powder patterns with few reflections.

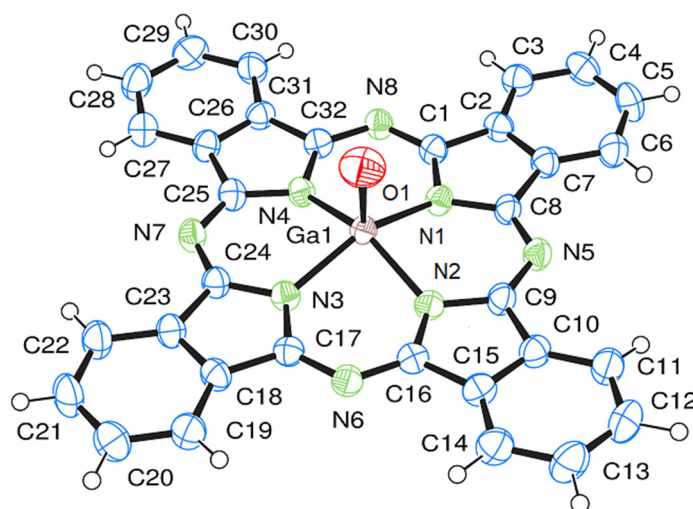


Figure 1. Asymmetric unit of $\text{GaO}_{0.5}\text{Pc}$ with atom labeling and thermal ellipsoids of 50%.

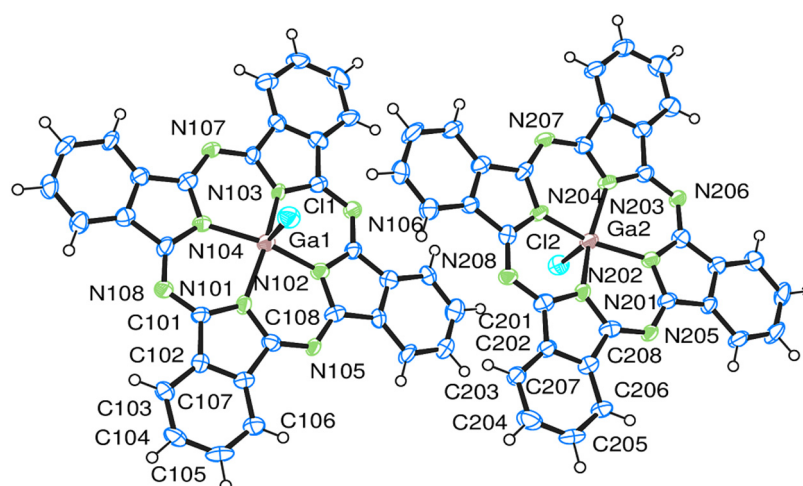


Figure 2. Two Pc molecules form the asymmetric unit of ClGaPc. Thermal ellipsoids of 50% and atom labeling following the numbering of Figure 1.

Table 2. Selected bond lengths [Å] for the asymmetric unit of PcGaOGaPc.

Ga1-O1	1.7336(6)
Ga1-N1	2.009(2)
Ga1-N2	2.012(3)
Ga1-N3	2.004(3)
Ga1-N4	2.003(3)
N1-C1	1.377(4)
N1-C8	1.386(4)
N2-C16	1.368(4)
N2-C9	1.376(4)
N3-C17	1.378(4)
N3-C24	1.381(4)
N4-C25	1.373(4)
N4-C32	1.378(4)
N5-C8	1.315(4)
N5-C9	1.322(4)
N6-C17	1.321(4)
N6-C16	1.327(4)
N7-C24	1.321(4)
N7-C25	1.323(4)
N8-C1	1.320(4)
N8-C32	1.335(4)

Table 3. Selected bond lengths [Å] for the two molecules in the asymmetric unit of GaClPc (solution a).

Ga1-N101	1.994(5)	Ga2-N201	1.987(5)
Ga1-N102	1.979(5)	Ga2-N202	1.989(5)
Ga1-N103	1.987(5)	Ga2-N203	1.987(5)
Ga1-N104	1.993(5)	Ga2-N204	1.992(5)
Ga1-Cl1	2.200(2)	Ga2-Cl2	2.197(2)
N101-C101	1.372(8)	N201-C201	1.380(8)
N101-C108	1.400(8)	N201-C208	1.390(8)
N102-C109	1.386(8)	N202-C209	1.382(8)
N102-C116	1.403(8)	N202-C216	1.397(8)
N103-C117	1.366(8)	N203-C217	1.381(8)
N103-C124	1.387(8)	N203-C224	1.377(8)
N104-C125	1.378(8)	N204-C225	1.381(8)
N104-C132	1.375(8)	N204-C232	1.368(8)
N105-C108	1.309(8)	N205-C208	1.328(8)
N105-C109	1.328(8)	N205-C209	1.324(8)
N106-C116	1.327(8)	N206-C216	1.326(8)
N106-C117	1.331(8)	N206-C217	1.328(8)
N107-C124	1.311(8)	N207-C224	1.324(8)
N107-C125	1.333(8)	N207-C225	1.331(8)
N108-C101	1.323(8)	N208-C201	1.344(8)
N108-C132	1.325(8)	N208-C232	1.320(8)

The asymmetric unit of PcGaOGaPc consists of one Pc molecule, which is linked by the P-1 symmetry of the space group through O to the symmetry-related Pc molecule, and both Pc molecules form a dimer, as depicted in Figure 3. The Ga-O bond length established in the dimeric molecule amounts to 1.7336(6) Å (for Al-O, 1.679 (2) Å) and both bond angles Ga-O-Ga and Al-O-Al amount to 180°. The staggering angle α of the two bisphthalocyanine planes is 0°. In his review on phthalocyanines, Engel [4,5] lists many bisphthalocyanine compounds of various conformations and cites that the angle α will be 0° if the distance of the two planes in the dimer is bigger than the van der Waals distance. The distance of the adjacent intermolecular planes is 3.47 Å for GaPc and 3.43 Å for AlPc (c.f. Table 4). The Ga atom lies 0.492 Å (Al 0.459 Å) above the isoindole nitrogen N1–N4 plane. The Pc rings of adjacent planes in the dimer are in an eclipsed conformation with an intraplanar spacing of 4.24 Å for GaPc and 4.13 Å for AlPc (c.f. Table 4). The data of Table 4 confirm the

isomorphous structure between PcGaOGaPc and PcAlOAlPc , with close values except for the bond lengths Ga-O and Al-O, of which the interactions with the stiff ring can be neglected.

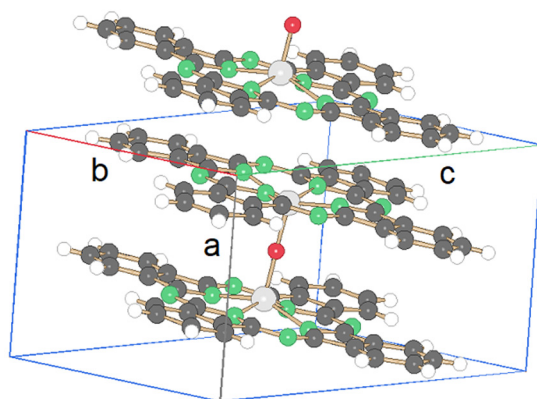


Figure 3. Stacking arrangement of neighboring $\text{GaO}_{0.5}\text{Pc}$ molecules.

In contrast, the second modification of ClGaPc , for which two solutions have been considered, contains two molecules in the asymmetric unit and shows a completely different arrangement in the unit cell of the $P-1$ space group (Figure 4). A projection down the a -axis reveals parallel planes formed by the four molecules present in the unit cell. The Ga-Cl bond length is 2.20 Å in both independent molecules of the asymmetric unit and Ga lies 0.439 Å above the isoindole nitrogen plane. These distances are collected in Table 4 with some further parameters and are compared with related Pc structures.

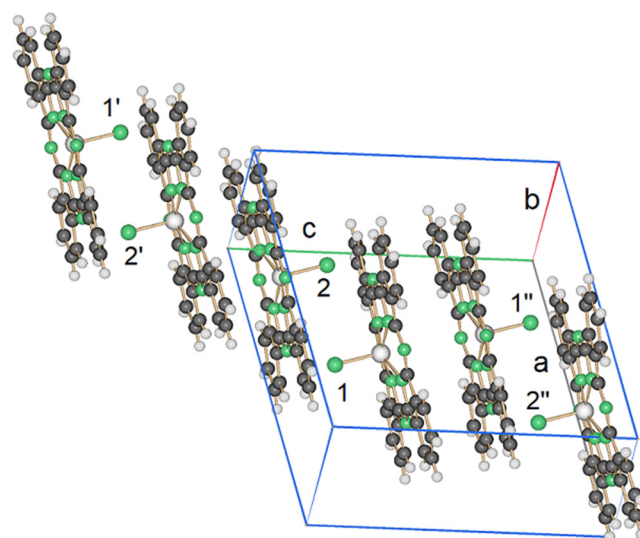


Figure 4. Arrangement of neighboring ClGaPc molecules (solution a), showing molecule 1 and 2 and symmetry-related ones 1', 2' and 1'', 2''.

The investigations of the two solutions for ClGaPc exhibit different disorder, as represented in Tables A2 and A3, but show quite similar conformations. They differ in the equivalent isotropic displacement parameters, U_{eq} , as well as in the anisotropic displacement parameters, U_{ij} matrix (c.f. CIF-files COD 300483, 300484), which could be a sign of distinct distortions of the first and second kind. In lattices affected by distortions of the first kind, the long-range periodicity of the atoms is preserved and included in the thermal matrix. In a lattice distortion of the second kind (paracrystallinity), the long-range order is lost, and each lattice point varies in position only in relation to its nearest neighbors and results in diminution of intensity and an increase in reflection breadth with increasing reflection angle, θ , and needs a special additional description [21]. The consideration of

such a disorder may provide the possibility of describing the differences obtained for the two modifications, a and b, of ClGaPc with a high Fourier peak of $1.21 \text{ e}/\text{\AA}^3$ when the reflections at larger reflection angles of sample b were included. In general, this disorder will cause changes. The maximum reflection angle, θ , of solution a extends to 20° that of solution b to 23° . The number of unique reflections differs by 2210 comparing solution a to b and, therefore, a big influence of the reflections at higher angles is expected.

The best approach for the disordered structure of ClGaPc seems to be solution a, where the temperature or disorder factor still represents a good approximation, and the coordinates describe the structure well with an R factor of 0.044 and the highest peak in difference Fourier reaching $0.54 \text{ e}/\text{\AA}^3$. The number of observed reflections with $I > 2\sigma(I)$ for both solutions surmounts, by far, the ones by Wynne [20] (c.f. Table 1).

The coordination of the metal atom M of all structures of Table 4 is square pyramidal with four coordinated nitrogen atoms at the basal apices and Cl or O occupying the remaining apex. The Pc molecules considered exhibit a plano-convex shape with a planar and a convex side which leads to different interactions of adjacent Pc planes of either planar—planar or convex—convex side representations.

Wynne [20] also studied a single-crystal structure of another polymorph of ClGaPc called ClGaPc 1, space group P-1, with only one Pc molecule in the asymmetric unit. In this structure Ga is centered $0.44 \text{ \AA}$ above the plane N1–N4. This structure compares well with all the data of the solutions a and b of ClGaPc listed in Table 4. $\text{GaO}_{0.5}\text{Pc}$ has a little longer distance, d_1 , with $0.49 \text{ \AA}$. The lengths of the Ga–N bonds are the same for solution a, b as listed in Table 3 and a small amount longer for $\text{GaO}_{0.5}\text{Pc}$ (Table 2). The Ga–Cl distance for solutions a and b is ca. $2.200 \text{ \AA}$ and compares well with the bond length of $2.217 \text{ \AA}$ for the Pc modification ClGaPc 1 [20]. The different interactions of the molecules in the two modifications cause differences in packing but has little effect on the conformation of the ClGaPc molecule.

Selected distances describing the conformation and packing of $\text{GaO}_{0.5}\text{Pc}$ and GaClPc are compared in Table 4 with the highly photosensitive TiOPc II [8] and HOGaPc V [2]. In contrast, both ClGaPc polymorphs are scarcely photosensitive. Table 4 also provides similar data for $\text{AlO}_{0.5}\text{Pc}$ compared with $\text{GaO}_{0.5}\text{Pc}$, except the distance, d_3 (M–O). These central atoms M and O atoms do not influence the packing of the Pc molecules in the unit cell. The data for HOGaPc V of Inami et al. [2] and a refinement resulting in an excellent approximation for a powder X-ray study have also been added in Table 4 for a comparison with the highly photosensitive TiOPc II.

The Ga–O bond and further bond lengths have been provided by an EXAFS determined structural study for PcGaOGaPc [9] and are also listed in Table 4. They show some differences compared with the geometrical data of this work. In particular, the Ga–O bond length, at $1.87(2) \text{ \AA}$ [9], differs significantly with the geometrical value of $1.7336(6) \text{ \AA}$ and to the theoretical quantum calculated value of $1.776 \text{ \AA}$ [10].

As demonstrated in Figure 3, the planar sides of the phthalocyanine rings of $\text{GaO}_{0.5}\text{Pc}$ are arranged parallel in this dimeric structure, with a distance $d = 3.47 \text{ \AA}$, compared with $3.25 \text{ \AA}$ for the two modifications, ClGaPc 1 and ClGaPc a and b (Table 4). Yet, a different overlap of the rings occurs for the two ClGaPc polymorphs when two adjacent rings are projected onto each other facing their planar sides. Figure 4 represents the stacking of the two independent molecules of the second modification for ClGaPc in the crystal structure with a distance $d = 3.25 \text{ \AA}$ between adjacent parallel and symmetry-related molecules 1 and $1''$, which also extends to molecule 2 and $2'$. The overlap resembles the stacking type observed for $\beta\text{-H}_2\text{Pc}$ [1] and provides low photosensitivity. The convex planes formed between adjacent molecules 1 and 2 deviate slightly from a parallel arrangement with $d^* \approx 3.38 \text{ \AA}$ and an overlap of these two molecules 1 and 2 is not observed. The crystal structures listed in Table 4 form stiff planes below and above the van der Waals distance, which, along with the π – π interactions of the atoms, is believed a necessary condition for photosensitivity.

Table 4. Selected distances describing the conformation and packing of GaO_{0.5}Pc and GaClPc as compared with related phthalocyanines determined by single-crystal analysis, except HOGaPcV, determined by a powder pattern.

Compound	d/Å	d*/Å	d ₁ /Å	d ₂ /Å	d ₃ /Å	d ₄ /Å			
						N1	N2	N3	N4
TiOPc II [8]	3.040	3.551	0.638	0.951	1.628	2.05	2.08	2.06	2.09
AlO _{0.5} Pc ⁺ [19]	3.431	4.127	0.459	0.384	1.680	1.99	1.98	1.97	1.97
GaO _{0.5} Pc ⁺ [22]	3.470	4.244	0.492	0.389	1.734	2.00	2.00	2.01	2.01
						N5	N6	N7	N8
HOGaPcV [11]	3.040	3.707	0.428	0.741	1.938	3.39	3.40	3.39	3.41
HOGaPcV [2]	3.060	3.452	0.531	0.892	1.843	2.00	2.03	2.00	2.03
GaClPc 1 [20]	3.248	3.331	0.440	0.519	2.218	1.98	1.98	1.98	1.99
GaClPc solution a [22]									
Molecule 1	3.250	1→2	0.439	0.533	2.200	1.99	1.98	1.99	1.99
Molecule 2	3.250	≈3.377 ^{&}	0.435	0.535	2.197	1.99	1.99	1.99	1.99
GaClPc solution b [22]									
Molecule 1	3.247	1→2	0.426	0.518	2.218	1.99	1.98	1.98	1.99
Molecule 2	3.252	≈3.377 ^{&}	0.432	0.520	2.216	1.99	2.00	1.98	1.98
EXAFS[PcGa] ₂ O [9]			0.45(9)		1.87(2)	2.02(2)	N _{aza}	3.33(4)	
(PcGa) ₂ O [10] (theory, mixed basis set, D _{4h} symmetry)					1.776	2.03			

⁺ dimer formed by Al–O–Al or Ga–O–Ga bonds, bond angles 180°. [&] no overlapping. d: distance between two adjacent nonpolar (planar)-facing parallel Pc planes (C1–C32). d*: distance between two adjacent polar parallel (convex)-facing Pc planes (C1–C32). d₁: distance between central atom M and the plane formed by the isoindole nitrogen N1–N4. d₂: distance between M and plane C1–C32. d₃: bond distance between central atom M and O, resp Cl. d₄: bond distance between central atom M and isoindole nitrogen N1...N4.

Possible profiles of representing adjacent overlaps of Pc polymorphs are illustrated in Figure 5. The stacking of neighboring planes of ClGaPc 1 is shown in Figure 5a. This overlap is comparable to that of the metal-free X-H₂Pc phthalocyanine polymorph [1] or TiOPc II [8], both of which show high photosensitivity but a long separation distance d is found. A similar pattern shows up for PcGaOGaPc (Figure 5b), with longer separation distances, d and d*, for possible effective π -interactions. Figure 5c shows the overlap of molecule 1 of the asymmetric unit with a symmetry-related molecule 1 for ClGaPc and Figure 5d shows the same type of overlap by molecule 2 with a symmetry-related molecule 2. The two representations look identical. These overlaps of the two independent ClGaPc molecules resemble that of the stacking type observed for β -H₂Pc [1] and provide low photosensitivity. An overlap of two adjacent independent molecules 1 and 2 of the asymmetric unit of ClGaPc is not observed (c.f. Figure 4).

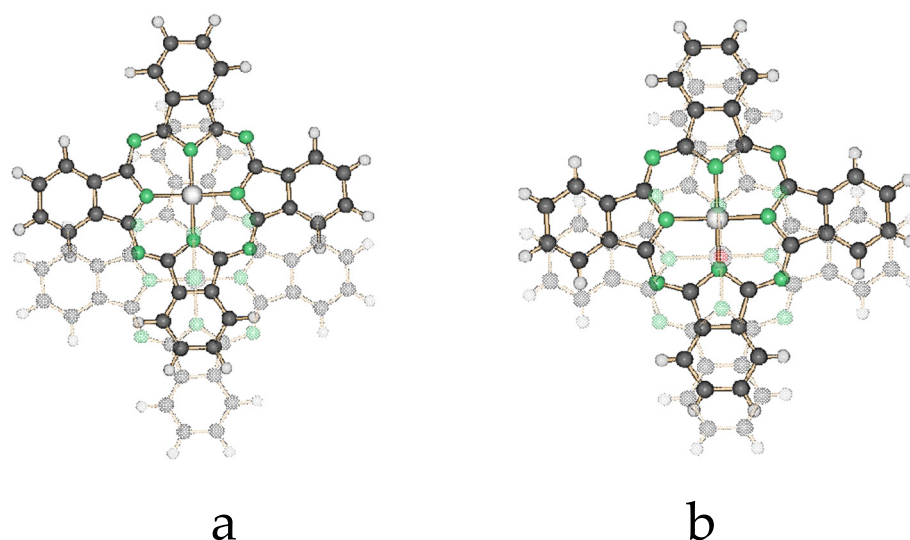


Figure 5. Cont.

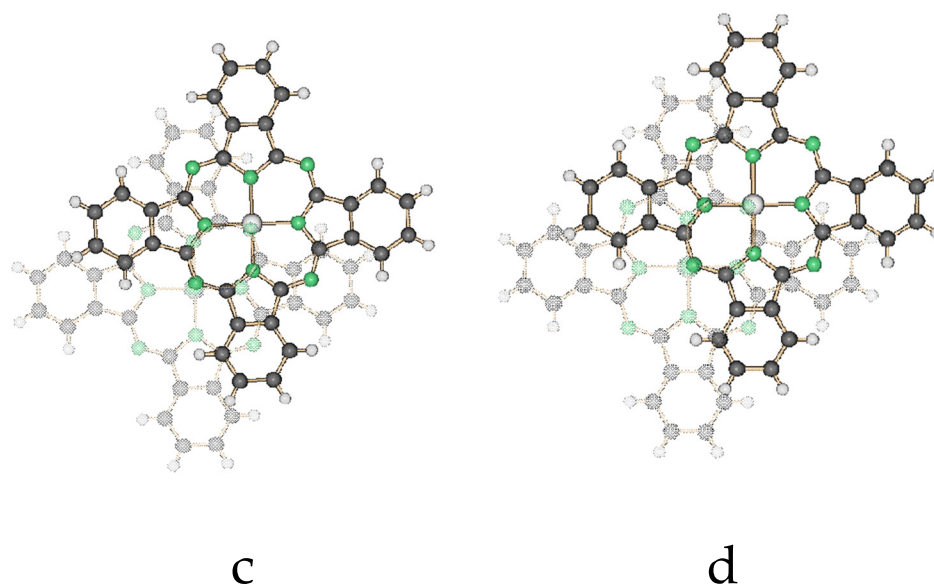


Figure 5. Projection of two adjacent Pc molecules with facing their planar sides onto the phthalocyanine plane. (a) ClGaPc 1, (b) GaO_{0.5} Pc, (c,d) the two independent molecules 1 and 2 of ClGaPc. Molecule 1 overlaps with molecule 1 (c), molecule 2 with 2 (d).

The packing of GaPc molecules in the crystallites provides a different picture of the interactions of molecular planes and is represented in Figure 6. GaOHPc V and also TiO II are assembled in staggered piles (Figure 6a). The molecular planes in the piles possess alternate distances, d and d^* , and adjacent molecules along the piles are arranged to exhibit the necessary overlap for excellent π -interactions. PcGaOGaPc also forms staggered piles with the neighboring pile, having the same form but lying behind the front stack in Figure 6b. The overlap of neighboring molecules of planar- or convex-facing sides is shown in Figure 3. The packing of ClGaPc 1 (Figure 6c) can best be described by the arrangement of parallel planes perpendicular to the extension of the planes forming molecules in which the single molecule 1 of the asymmetric unit is present as well as the symmetry related one 1'. The distance between the planes alternates from d and d^* , with planar-facing sheets between molecule 1 and inversion symmetry-related ones 1' and convex-facing sheets between molecule 1 and 1'. Adjacent molecules with planar-facing sides show the overlap represented in Figure 5a, adjacent convex molecules are not overlapped. The two independent molecules a and b of ClGaPc (Figure 6d) are also placed in sheets as shown for ClGaPc 1 in Figure 6c but rotated within the pile and show an overlap appearance represented in Figure 5c,d. The same distance $d = 3.25 \text{ \AA}$ occurs between molecule 1 and molecule 1 as well as between molecule 2 and 2. Despite the short distance between the adjacent molecules, little photosensitivity is observed due to the almost absent π -interaction. The distances, d and d^* , of the represented planes in Figure 6d alternate according to the facing of the planar or convex sides between sheets formed by the adjacent molecules 1 or 2. No overlap is observed between neighboring molecules 1 and 2 of distance d^* , as demonstrated also in Figure 6c.

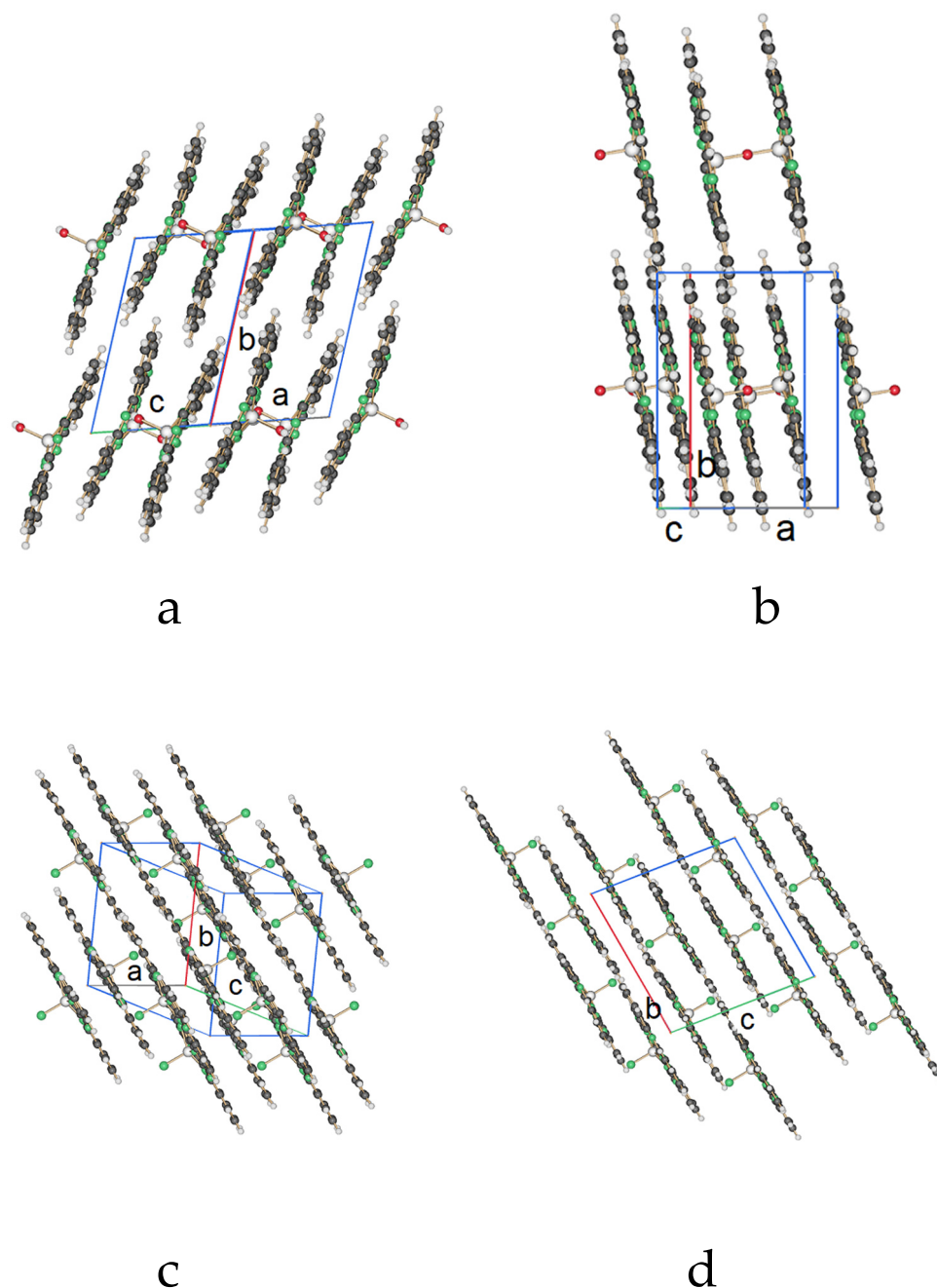


Figure 6. Representation of the packing of various Pc molecules in crystallites. (a) GaOHPC V, (b) PcGaOGaPc, (c) ClGaPc 1, (d) ClGaPc solution a.

4. Conclusions

An evaluation of the structural property relationship of photosensitive phthalocyanine pigments requires the interaction of neighboring molecules to be known. An excellent method for establishing the geometry of the molecular structures is a single-crystal structure determination.

The crystal structure of two Ga-phthalocyanines has been determined by single-crystal X-ray investigations and found that the adjacent stiff planes of the molecules are arranged in differently stacked planes, both of which are considered to result in low photosensitivity. In addition, the structural data could be used for further considerations. It was noticed that the two phthalocyanines, PcGaOGaPc and the second modification ClGaPc, are isomorphous with the Al-Pcs, PcAlOAlPc and ClAlPc, with almost identical unit cells of the crystal structures. Furthermore, PcGaOGaPc and PcAlOAlPc exhibit almost the same molecular

packing arrangement. This observation led to the conclusion that the few interactions exerted by the central atoms can be neglected for packing investigations. The single-crystal data for ClAlPc from Wynne [20] are not precise enough for a comparison with the single-crystal structural data determined for ClGaPc. However, these ClGaPc data can be used for a prediction of the packing for the ClAlPc molecules. The proposed method has been applied for a structural determination of a phthalocyanine with a given unit cell and few X-ray powder data and demonstrated for HOGaPC V.

The difference in X-ray intensities for the ClGaPc modification with two molecules, a and b, in the asymmetric unit is probable due to disorder of the second kind. Yet, the determined disordered crystalline structure of this material exhibits a slightly higher density than ClGaPc 1 and can be regarded as the more stable form.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst14020182/s1>.

Funding: This research received no external funding.

Data Availability Statement: Data are contained within the article and (Crystallography Open Database) COD 300042, 300483, 300484.

Acknowledgments: The author acknowledges generous support by the Xerox foundation, thanks James Duff for providing the samples and Terry L. Bluhm for stimulation discussions.

Conflicts of Interest: The author declares no conflict of interest.

Appendix A

Table A1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the asymmetric unit of PcGaOGaPc. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	X	y	z	U(eq)
Ga1	2849(1)	4766(1)	5120(1)	29(1)
O1	5000	5000	5000	63(1)
N1	1643(3)	6037(2)	4467(2)	34(1)
N2	2072(3)	3961(2)	3781(2)	34(1)
N3	2831(3)	3357(2)	5840(2)	32(1)
N4	2408(3)	5430(2)	6515(2)	33(1)
N5	1421(3)	5457(2)	2633(2)	37(1)
N6	2794(3)	2165(2)	4317(2)	37(1)
N7	3216(3)	3960(2)	7662(2)	38(1)
N8	1763(3)	7244(2)	5979(2)	36(1)
C1	1538(4)	7020(3)	4958(3)	34(1)
C2	1167(4)	7827(3)	4162(3)	36(1)
C3	938(5)	8921(3)	4251(3)	42(1)
C4	653(5)	9484(3)	3331(3)	50(1)
C5	612(5)	8969(3)	2358(3)	53(1)
C6	831(5)	7877(3)	2259(3)	46(1)
C7	1108(4)	7312(3)	3188(3)	37(1)
C8	1397(4)	6187(3)	3388(3)	33(1)
C9	1719(4)	4437(3)	2820(3)	36(1)
C10	1782(4)	3634(3)	1989(3)	37(1)
C11	1555(5)	3704(3)	900(3)	44(1)
C12	1776(5)	2791(3)	310(3)	54(1)
C13	2190(5)	1828(4)	796(3)	54(1)
C14	2399(5)	1751(3)	1878(3)	47(1)
C15	2196(4)	2671(3)	2475(3)	37(1)
C16	2370(4)	2899(3)	3603(3)	36(1)
C17	2991(4)	2381(2)	5340(3)	33(1)

Table A1. *Cont.*

	X	y	z	U(eq)
C18	3472(4)	1584(3)	6125(3)	36(1)
C19	3761(5)	496(3)	6033(3)	42(1)
C20	4182(5)	−57(3)	6948(3)	51(1)
C21	4309(5)	465(3)	7922(3)	53(1)
C22	4036(5)	1549(3)	8023(3)	46(1)
C23	3594(4)	2104(3)	7102(3)	37(1)
C24	3199(4)	3219(3)	6910(3)	34(1)
C25	2851(4)	4973(3)	7473(3)	35(1)
C26	2884(4)	5789(3)	8304(2)	36(1)
C27	3254(5)	5743(3)	9383(3)	44(1)

Table A2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the second modification of GaCl, solution a. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ga1	5073(1)	4016(1)	6637(1)	33(1)
Ga2	683(1)	−716(1)	8360(1)	32(1)
Cl1	5650(1)	4278(1)	8310(1)	42(1)
Cl2	104(1)	−965(1)	6689(1)	42(1)
N101	4336(4)	5233(4)	6306(4)	30(1)
N102	3708(4)	3351(4)	6322(4)	31(1)
N103	5588(4)	2707(4)	6298(4)	28(1)
N104	6221(4)	4591(4)	6289(4)	29(1)
N105	2637(4)	4757(4)	6330(4)	29(1)
N106	4159(4)	1638(4)	6252(4)	31(1)
N107	7275(4)	3173(4)	6292(4)	31(1)
N108	5723(4)	6281(4)	6229(4)	32(1)
N201	174(4)	597(4)	8695(4)	30(1)
N202	−457(4)	−1287(4)	8718(4)	30(1)
N203	1419(4)	−1930(4)	8682(4)	31(1)
N204	2051(4)	−36(4)	8670(4)	29(1)
N205	−1492(4)	134(4)	8784(4)	29(1)
N206	11(4)	−2990(4)	8706(4)	30(1)
N207	3127(4)	−1448(4)	8740(4)	34(1)
N208	1579(4)	1659(4)	8657(4)	32(1)
C101	4793(5)	6105(5)	6268(5)	31(2)
C102	4067(5)	6880(5)	6258(5)	32(2)
C103	4149(5)	7888(4)	6228(5)	38(2)
C104	3302(6)	8417(5)	6206(5)	44(2)
C105	2392(6)	7971(6)	6196(5)	46(2)
C106	2310(5)	6993(5)	6237(5)	38(2)
C107	3161(5)	6443(4)	6273(4)	31(2)
C108	3333(5)	5394(5)	6310(4)	30(2)
C109	2808(5)	3806(5)	6315(5)	35(2)
C110	2037(5)	3076(5)	6253(5)	32(2)
C111	1012(5)	3156(5)	6222(6)	44(2)
C112	455(6)	2315(6)	6132(6)	52(2)
C113	854(6)	1417(6)	6072(5)	49(2)
C114	1865(5)	1314(5)	6109(5)	38(2)
C115	2458(5)	2175(5)	6212(5)	36(2)
C116	3499(5)	2341(5)	6248(4)	29(2)
C117	5116(5)	1827(5)	6277(5)	31(2)
C118	5830(5)	1044(4)	6271(5)	33(2)
C119	5730(5)	46(5)	6259(5)	43(2)

Table A2. Cont.

	x	y	z	U(eq)
C120	6560(6)	−506(5)	6240(5)	52(2)
C121	7461(5)	−68(5)	6229(5)	43(2)
C122	7573(5)	925(5)	6246(5)	42(2)
C123	6738(5)	1483(4)	6269(4)	30(2)
C124	6577(5)	2526(5)	6293(4)	27(2)
C125	7103(5)	4124(5)	6277(4)	33(2)
C126	7857(5)	4840(5)	6246(5)	31(2)
C127	8859(5)	4745(5)	6239(5)	40(2)
C128	9386(5)	5580(5)	6209(5)	45(2)
C129	8948(5)	6494(5)	6182(5)	42(2)
C130	7962(5)	6584(5)	6196(5)	36(2)
C131	7415(5)	5745(5)	6224(4)	31(2)
C132	6371(5)	5568(5)	6240(5)	32(2)
C201	625(5)	1487(5)	8678(4)	32(2)
C202	−71(5)	2257(5)	8716(5)	31(2)
C203	16(5)	3264(5)	8715(5)	42(2)
C204	−800(6)	3804(5)	8755(6)	51(2)
C205	−1695(5)	3375(5)	8798(5)	43(2)
C206	−1788(5)	2389(5)	8810(5)	33(2)
C207	−955(5)	1832(5)	8768(5)	32(2)
C208	−796(5)	790(5)	8759(4)	33(2)
C209	−1334(5)	−816(5)	8754(5)	32(2)
C210	−2096(5)	−1538(4)	8766(4)	29(2)
C211	−3102(5)	−1458(5)	8784(5)	38(2)
C212	−3628(5)	−2274(6)	8805(5)	46(2)
C213	−3196(5)	−3169(5)	8816(5)	43(2)
C214	−2211(5)	−3269(5)	8785(5)	38(2)
C215	−1653(5)	−2445(5)	8765(4)	30(2)
C216	−642(5)	−2285(5)	8720(5)	32(2)
C217	959(5)	−2813(5)	8706(5)	32(2)
C218	1702(5)	−3575(5)	8760(5)	32(2)
C219	1627(6)	−4564(5)	8804(5)	44(2)
C220	2480(6)	−5089(5)	8890(6)	54(2)
C221	3393(6)	−4657(5)	8927(6)	48(2)
C222	3488(5)	−3672(5)	8887(5)	40(2)
C223	2611(5)	−3123(4)	8795(5)	32(2)
C224	2419(5)	−2100(5)	8739(5)	30(2)
C225	2944(4)	−504(5)	8697(4)	31(2)
C226	3723(5)	216(5)	8718(4)	33(2)
C227	4724(5)	126(5)	8734(5)	40(2)
C228	5289(5)	966(6)	8784(5)	49(2)
C229	4857(6)	1874(5)	8779(5)	44(2)
C230	3848(5)	1970(5)	8745(5)	37(2)
C231	3279(5)	1126(5)	8704(4)	29(2)
C232	2219(5)	943(5)	8671(4)	31(2)

Table A3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the second modification of GaCl, solution b. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ga1	5070(1)	4015(1)	6626(1)	28(1)
Ga2	688(1)	−714(1)	8371(1)	28(1)
Cl1	5654(1)	4274(1)	8314(1)	37(1)
Cl2	100(1)	−965(1)	6685(1)	37(1)
N101	4339(4)	5230(4)	6304(4)	30(1)
N102	3704(4)	3348(4)	6324(4)	30(1)

Table A3. Cont.

	x	y	z	U(eq)
N103	5585(4)	2705(4)	6300(4)	29(1)
N104	6217(4)	4583(4)	6279(4)	30(1)
N105	2649(4)	4761(4)	6326(4)	33(1)
N106	4160(4)	1640(4)	6242(4)	34(1)
N107	7282(4)	3174(4)	6289(4)	33(1)
N108	5727(4)	6274(4)	6231(4)	31(1)
N201	166(4)	599(4)	8703(4)	31(1)
N202	−465(4)	−1285(4)	8716(4)	31(1)
N203	1426(4)	−1922(4)	8702(4)	31(1)
N204	2054(4)	−43(4)	8679(4)	32(1)
N205	−1493(4)	138(4)	8781(4)	33(1)
N206	16(4)	−2986(4)	8702(4)	33(1)
N207	3128(4)	−1446(4)	8745(4)	33(1)
N208	1579(4)	1654(4)	8668(4)	33(1)
C101	4802(5)	6110(5)	6265(5)	31(2)
C102	4069(5)	6877(5)	6256(5)	32(2)
C103	4156(6)	7878(4)	6228(5)	37(2)
C104	3322(6)	8399(5)	6207(6)	46(2)
C105	2407(6)	7972(6)	6201(6)	45(2)
C106	2318(6)	6988(5)	6229(6)	40(2)
C107	3169(5)	6439(5)	6266(5)	35(2)
C108	3348(5)	5402(5)	6304(5)	32(2)
C109	2819(5)	3806(5)	6320(5)	33(2)
C110	2026(5)	3086(5)	6248(5)	33(2)
C111	1038(6)	3167(5)	6242(6)	45(2)
C112	448(7)	2324(6)	6128(6)	54(2)
C113	861(6)	1414(6)	6081(6)	45(2)
C114	1873(6)	1323(5)	6106(5)	40(2)
C115	2466(6)	2173(5)	6207(5)	36(2)
C116	3507(5)	2340(5)	6248(5)	33(2)
C117	5105(6)	1809(5)	6276(5)	33(2)
C118	5825(6)	1039(5)	6259(5)	36(2)
C119	5721(6)	43(5)	6258(6)	40(2)
C120	6552(6)	−503(5)	6240(6)	49(2)
C121	7463(7)	−82(6)	6227(6)	49(2)
C122	7577(6)	928(5)	6253(6)	40(2)
C123	6744(5)	1479(5)	6269(5)	33(2)
C124	6559(5)	2535(4)	6288(5)	28(2)
C125	7098(5)	4120(4)	6266(5)	29(2)
C126	7856(5)	4830(5)	6247(5)	32(2)
C127	8863(6)	4740(6)	6238(6)	47(2)
C128	9404(6)	5572(6)	6213(6)	49(2)
C129	8946(7)	6475(6)	6193(6)	48(2)
C130	7965(5)	6574(5)	6205(5)	36(2)
C131	7415(5)	5739(5)	6212(5)	33(2)
C132	6385(5)	5566(5)	6242(5)	30(2)
C201	640(5)	1483(5)	8685(5)	31(2)
C202	−62(5)	2245(5)	8721(5)	33(2)
C203	11(6)	3270(5)	8719(6)	46(2)
C204	−786(6)	3799(5)	8754(6)	47(2)
C205	−1696(6)	3372(6)	8795(6)	46(2)
C206	−1793(6)	2384(5)	8798(5)	38(2)
C207	−951(5)	1827(5)	8764(5)	33(2)
C208	−797(5)	783(5)	8756(5)	29(2)
C209	−1330(5)	−819(5)	8760(5)	30(2)
C210	−2093(5)	−1536(5)	8770(5)	31(2)
C211	−3090(5)	−1433(5)	8786(5)	37(2)
C212	−3618(6)	−2263(6)	8809(6)	50(2)

Table A3. Cont.

	x	y	z	U(eq)
C213	−3196(6)	−3177(6)	8812(6)	42(2)
C214	−2201(6)	−3278(5)	8793(5)	39(2)
C215	−1650(5)	−2437(5)	8758(5)	33(2)
C216	−641(5)	−2280(5)	8721(5)	31(2)
C217	948(5)	−2804(5)	8703(5)	33(2)
C218	1695(5)	−3570(5)	8755(5)	35(2)
C219	1607(6)	−4557(5)	8790(6)	46(2)
C220	2463(6)	−5095(5)	8880(6)	51(2)
C221	3399(7)	−4661(5)	8931(6)	50(2)
C222	3470(6)	−3665(5)	8871(6)	40(2)
C223	2615(6)	−3126(5)	8800(5)	36(2)
C224	2406(5)	−2095(4)	8738(5)	28(2)
C225	2943(5)	−500(5)	8707(5)	29(2)
C226	3713(5)	218(5)	8711(5)	35(2)
C227	4727(6)	122(6)	8750(6)	44(2)
C228	5283(6)	962(6)	8774(6)	46(2)
C229	4857(6)	1875(5)	8791(6)	45(2)
C230	3846(6)	1964(5)	8746(6)	42(2)
C231	3279(5)	1125(5)	8714(5)	32(2)
C232	2219(5)	941(4)	8676(5)	29(2)

References

- Oka, K.; Okada, O. Study of the Relationship between Crystal Structure and Photosensitivity of Phthalocyanine Pigments. *J. Imaging Sci. Technol.* **1993**, *37*, 607–609.
- Inami, K.; Oka, K.; Daimon, K. Crystal Structure of Hydroxy Gallium Phthalocyanine by Rietveld Analysis. *J. Imaging Sci. Technol.* **1995**, *39*, 298–302.
- Daimon, K.; Nukuda, K.; Sakaguchi, Y.; Igarashi, R. A new Polymorph of Hydroxygallium Phthalocyanine and its Application in a Photoreceptor. *J. Imaging Sci. Technol.* **1996**, *40*, 249–253. [\[CrossRef\]](#)
- Engel, M.K. *Single-Crystal and Solid-State Molecular Structures of Phthalocyanine Complexes*; Report Kawamura Institute Chemical Research: Sakado, Japan, (Vol. Date 1996); 1997; pp. 11–54.
- Engel, M.K. Single-Crystal Structures of Phthalocyanine Complexes and Related Macrocycles 122. In *The Porphyrin Handbook, Phthalocyanines: Structural Characterization*; Kadish, K.M., Smith, K.M., Guillard, R., Eds.; Academic Press: New York, NY, USA, 2003; Volume 20, pp. 1–88.
- Yamasaki, K.; Okado, O.; Inami, K.; Oka, K.; Kotani, M.; Yamada, H. Gallium Phthalocyanines: Structure Analysis and Electroabsorption Study. *J. Phys. Chem.* **1997**, *101*, 13–19. [\[CrossRef\]](#)
- Okada, Y.; Hoshi, T.; Kobayashi, N. Recent Progress in Optically-Active Phthalocyanines and Their Related Azamacrocycles. *Front. Chem.* **2020**, *8*, 595998. [\[CrossRef\]](#)
- Hiller, W.; Straehle, J.; Kobel, W.; Harnack, M. Polymorphie, Leitfähigkeit und Kristallstrukturen von Oxo-phthalocyaninato-titan (IV). *Z. Krist.* **1982**, *159*, 173–183. [\[CrossRef\]](#)
- Chen, Y.; Hanack, M.; Arakic, Y.; Itoc, O. Axially modified gallium phthalocyanines and naphthalocyanines for optical limiting. *Chem. Soc. Rev.* **2005**, *34*, 517–529. [\[CrossRef\]](#) [\[PubMed\]](#)
- Semenov, S.G.; Bedrina, M.E. A Quantum Chemical Study of Gallium(III) (μ -oxo)bis[phthalocyaninate] and Gallium(III) (μ -oxo)bis[perfluorophthalocyaninate] Molecules. *J. Struct. Chem.* **2017**, *58*, 441–446. [\[CrossRef\]](#)
- Zugenmaier, P. *Structural Investigations on Hydroxygallium Phthalocyanine Type V (HOGaPc V)*; Institut für Physikalische Chemie der TU Clausthal: Clausthal-Zellerfeld, Germany, 2024.
- Zugenmaier, P.; Sarko, A. Packing Analysis of Carbohydrates and Polysaccharides I. Monosaccharides. *Acta Cryst.* **1972**, *B28*, 3158–3166. [\[CrossRef\]](#)
- Fair, C.K. *MolEN: An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.
- Burla, M.C.; Caliendo, R.; Carrozzini, B.; Cascarano, G.L.; Cuocci, C.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G. Crystal structure determination and refinement via SIR2014. *J. Appl. Cryst.* **2015**, *48*, 306–309. [\[CrossRef\]](#)
- Sheldrick, G.M. *SHELX-97: A Program for the Refinement of Single-Crystal Diffraction Data*; University of Göttingen: Göttingen, Germany, 1997.
- Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.
- Keller, E. *SCHAKAL99: A Computer Program for the Graphic Representation of Molecular and Crystallographic Models*; Kristallographisches Institut der Universität: Freiburg i.Br., Germany, 1999.
- Farrugia, L.J. WinGX and ORTEP for Windows: An update. *J. Appl. Cryst.* **2012**, *45*, 849–854. [\[CrossRef\]](#)

19. Wynne, K.J. Two Ligand-Bridged Phthalocyanines: Crystal and Molecular Structure of Fluoro(phthalocyaninato)gallium(III), $[\text{Ga}(\text{Pc})\text{F}]_n$, and $(\mu\text{-Oxo})\text{bis}[(\text{phthalocyaninato})\text{-aluminum(III)}]$, $[\text{Al}(\text{Pc})]_2\text{O}$. *Inorg. Chem.* **1985**, *24*, 1339–1343. [[CrossRef](#)]
20. Wynne, K.J. Crystal and Molecular Structure of Chloro(phthalocyaninato)gallium (III), $\text{Ga}(\text{Pc})\text{Cl}$, and Chloro(phthalocyaninato)aluminium (III), $\text{Al}(\text{Pc})\text{Cl}$. *Inorg. Chem.* **1984**, *23*, 4658–4663. [[CrossRef](#)]
21. Alexander, L.E. *X-ray Diffraction Methods in Polymer Science*; John Wiley & Sons, Inc.: New York, NY, USA, 1969; pp. 423–429.
22. Zugenmaier, P. *Report on Structural Investigations on Pigments*; Xerox Chemical Analysis Area: Webster, NY, USA, 1998.

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